

ISOBARIC VAPOUR LIQUID EQUILIBRIA OF HYDROCARBON-  
ALCOHOL SYSTEMS

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of

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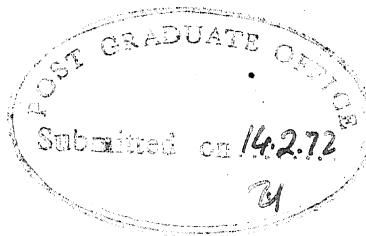
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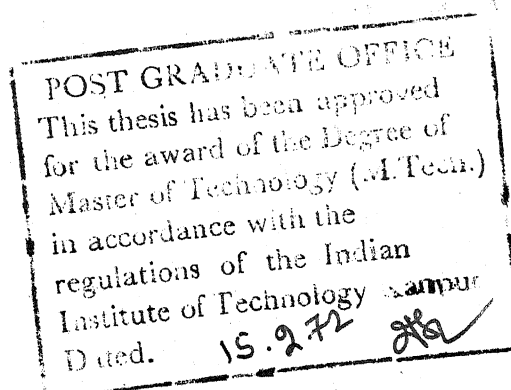
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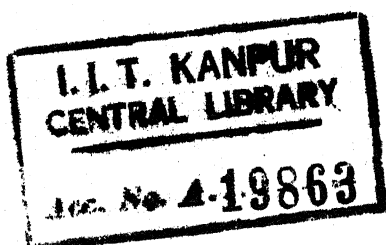
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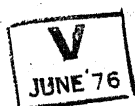
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NOMENCLATURE

1	Activity Coefficient of Component 1 in a liquid mixture of 1 and 2.
2	Activity Coefficient of Component 2 in a liquid mixture of 1 and 2.
$P_1^0$	Vapour pressure for Component 1
$P_2^0$	Vapour pressure for Component 2
$G^E$	Excess Free Energy of Mixing
	Uncertainty in Calculation.
A, B, C	Antoine's Constants
$B_{ij}$	Cross Virial Coefficient of Components i and J.
$v_1$	Molar Volume of Component 1.
$v_2$	Molar Volume of Component 2.
R	Gas Constant
T	Temperature

ABSTRACT

The isobaric vapour liquid equilibrium data have been measured for the systems (i) Methylcyclohexanol + n-heptane and (ii) Toluene + n-Heptanol at a pressure of 760 mm.Hg. The equilibrium still, as designed by Yerazunis, Flowright and Smola has been used for this purpose after some modifications. The data have been tested for thermodynamic consistency using Herington's area test. The isobaric vapor liquid equilibrium data have been calculated using the Malesinski's method from a single experimental data. These data have then been compared with experimentally measured data for testing the validity of the Malesinski's method for prediction of isobaric vapour liquid equilibrium data of hydrocarbon + alcohol systems. Since the vapor pressure data for methylcyclohexanol were not available in the literature, the vapour pressure data have been measured over a pressure range of 200 - 800 mm Hg by using the twin ebulliometric method and the data have been correlated for Martin's equation.

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## CHAPTER I

### INTRODUCTION

A knowledge of the phase equilibrium properties is frequently required in chemical engineering plant operations. In each of these plant operations there is transfer of a component or a group of components from one phase to another. This occurs because when the two phases are brought into contact, they tend to exchange their constituents until the phases are in equilibrium i.e. the composition of each phase attains a constant value. The equilibrium composition of two phases are different from each other and it is this difference which enables separation of mixtures by distillation, extraction etc. Phase equilibrium thermodynamics seeks to establish the relations between the various properties which ultimately prevail when two phases reach a state of equilibrium with each other.

Most of the liquids are non-ideal in nature and their vapour liquid equilibrium data cannot be directly obtained from Raoult's Law and Dalton's Law of partial pressures. Hence the vapour liquid equilibrium data for these systems are either determined experimentally or predicted using molecular theories of solutions. Since at the present time the molecular theories of solutions can not predict accurately the vapour liquid equilibrium data for a wide range of systems, it is necessary to improve the existing theories of solutions. For this purpose also it is needed to compile experimental data of various representative systems so that validity of these

theories can be tested with the experimental data before they can actually be applied. The determination of vapour liquid equilibrium data can be carried out either at constant pressure or at constant temperature. In this work isobaric vapour liquid equilibrium data have been investigated for two binary systems.

Out of several factors contributing to non-ideality of a mixture of liquids two important factors are (i) Force of attraction between like and unlike molecules and (ii) Size difference between the two constituent molecules. Firstly the forces of attraction between unlike molecules are quantitatively different from those between like molecules, giving rise to a non vanishing heat of mixing. Secondly, if the unlike molecules differ significantly in size or shape, the molecular arrangement in the mixture is appreciably different from that of the pure liquids, giving rise to a non-ideal entropy of mixing. Finally, in a binary mixture, if the forces of attraction between one of three possible pair interactions are very much different in magnitude from those of the other two, certain preferred orientations of the molecules in the mixture may induce phase separation or formation of azeotropes.

Non-ideality in liquid solutions results from the molecular interactions between its constituent molecules and thus can be explained in terms of intermolecular forces existing between them. There are different types of intermolecular forces but for the present purpose only a few important ones



contributing to the non-ideality of the mixture of polar and non-polar liquids are cited.

A non polar molecule has no permanent dipole moment but when such a molecule is subjected to an electric field, the electrons are displaced from their ordinary positions and a dipole is induced. When a non-polar molecule is situated in an electric field, set up by the presence of a nearby polar molecule, the resultant force between the permanent and induced dipole is always attractive. This attractive force explains the nature of intermolecular force existing between the polar and the non-polar liquids.

The non-ideal behaviour of liquid mixtures of polar and non-polar components can also be interpreted in terms of association. By association it is meant the association of polar components to dimers, trimers etc. The concentration of the new chemical species formed are related to those of monomers by the equilibrium constants of the law of mass action. As a result, the forces of interaction between one of three possible pair interactions are very much stronger than those of the other two, which may induce non-ideality.

In the present work the main aim is to study the non-ideality of liquid mixtures due to a large difference in the forces of attraction between the like and unlike constituent molecules essentially of the same molecular size. Thus mixtures of the present study have been chosen to comprise a  $C_7$ (polar) alcohol and  $C_7$ (nonpolar) hydrocarbon so that H-OH interaction can be studied. The systems selected for this work are:

(i)(Methylcyclohexanol + n-heptane) and (ii)(Toluene+n-heptanol).

## CHAPTER II

### REVIEW OF LITERATURE

Vapour liquid equilibrium data can be obtained by two methods namely, (i) static method (ii) Dynamic method. The static method involves measurement of dew point and bubble point pressures at a constant temperature whereas the dynamic method involves measurement of equilibrium liquid and vapour compositions at constant pressure. For static method of equilibrium studies PVT data are measured whereas for dynamic method an equilibrium still is used for separation of a liquid sample in equilibrium with a vapour sample.

Vapour liquid equilibrium data can be obtained either by distillation method or by a method involving circulation of only vapour phase or circulation of both vapour and liquid phases. A literature survey indicates that although the first equilibrium still with circulation of the vapor phase was proposed by Jamaguchi and Sameshima, the first equilibrium still which functioned satisfactorily was constructed by Othmer<sup>(26)</sup>. Over the recent years Othmer's still has undergone several modifications. In fact, Othmer, in an effort to remove some of the weaknesses of his original set-up, proposed several modifications. A statistical evaluation of the data obtained from the modified Othmer's still shows that the results obtained are to varying extent subject to errors arising from several sources. Jones and his coworkers<sup>(26)</sup> later improved the design of the modified Othmer still.

But the incorrect measurement of boiling point is a drawback in the stills having a circulating vapour phase as in the Othmer still, Jones still etc. This error was eliminated in the stills with circulation of both vapour and liquid phases and the first equilibrium still of this type was proposed by Gillespie<sup>(26)</sup>. However, the drawback of this still lies in the relatively long period for the attainment of equilibrium and in fact, Gillespie himself pointed out some serious errors in his still. These errors led to several modifications of the original Gillespie still such as proposed<sup>(26)</sup> by Fowler, Altsheler, Rose Williams, Ellis, Scatchard, etc. The equilibrium still used for the present investigation is a modification of Gillespie still and it was developed by Yearazunis, Flowright and Smola.<sup>(18)</sup>

Various authors have studied Vapour liquid equilibrium of hydrocarbon + alcohol systems using different equilibrium stills. A detailed survey of literature reveals that in 1912 Dan Tyrer<sup>1</sup> obtained the vapour liquid equilibrium data for the mixture of (ethyl alcohol and benzene). The method employed to determine the composition of the vapour which boils off from a mixture of two liquids of known composition consists in determining the density of the vapour. From this the composition was calculated by assuming the validity of the additive law for mixed vapours. The mixture did not form any azeotrope. It has been observed that at low compositions the vapour is richer in the heavier constituent than the liquid; but at a higher compositions the reverse is true. In 1933, Martin and

Collie<sup>(2)</sup> determined the isothermal vapour liquid equilibrium data for phenol + benzene system. Apparatus with circulation of vapour phase is used for this purpose. No azeotrope was formed. In 1945, M. Benedict and coworkers<sup>(4)</sup> determined the isobaric vapour liquid equilibrium data for MeOH + n-heptane and MeOH + toluene. The unit used for this purpose was a batch distillation unit. Both the mixtures were analysed refractometrically on a valentine refractometer having a precision of  $\pm 0.00003$  units. It was found experimentally that at atmospheric pressure heptane and methanol containing 74.7% MeOH form a minimum boiling azeotrope at 58.8°C whereas methanol and toluene containing 88 mole% MeOH form an azeotropic mixture boiling at 63.6°C. In the same year Harry G. Drickamer and G.G. Brown<sup>5</sup> obtained vapour liquid equilibrium data at atmospheric pressure for the systems (toluene + phenol), (methylcyclohexane + phenol), (isooctane + phenol, (isononane + phenol); The equilibrium still used for most of the work was essentially similar to one described by Othmer.<sup>26</sup> Another equilibrium still similar to the one described by Jones, Schoenborn and Colburn<sup>26</sup> was also used for part of the work. The results obtained on the two stills check within the experimental accuracy of each unit. The phenol-isooctane data are not reliable above 10% phenol in liquid phase because of limited solubility of phenol in paraffinic hydrocarbons. Similarly methylcyclohexane-phenol data are unreliable above 30% phenol in liquid phase. In addition, vapour liquid equilibrium data for isononane-phenol was obtained at low phenol concentration.

In 1952, Savitt and D.F. Othmer<sup>6</sup> determined the vapour liquid equilibrium data for benzene-p-cresol system. The data were obtained by modified Othmer still<sup>26</sup> as pointed out by Othmer himself. The mixture did not form any azeotrope and hence the separation is fairly simple. In 1960, J.E. Sinor and J.H. Weber<sup>8</sup> determined isobaric vapour liquid equilibrium data for (ethyl alcohol-hexane) and EtOH-methylcyclopentane system. Jones<sup>26</sup> still (which is a modification of othmer still) has been used for this purpose. For both the systems it was found that at low compositions the vapour is richer in the heavier constituent than the liquid. But at higher compositions the reverse is true. The systems did not form any azeotrope. In 1961, S.R.M. Ellis and M.J. Spurr<sup>11</sup> determined isobaric vapour liquid equilibrium data for the systems (ethyl alcohol-ethyl benzene) and (ethyl alcohol-decane). The Ellis still<sup>26</sup> was used. This is an equilibrium still with circulation of both vapour and liquid phases. The samples were analyzed by accurate refractive index measurements. In 1963, P.S. Prabhu and Mathew Van Winkle<sup>15</sup> determined vapour liquid equilibrium data for the systems n-hexane-1-propanol at 760 mm Hg. using a modified Colburn still.<sup>26</sup> Temperatures were measured using a Cu-constantan thermocouple. The vapour and liquid samples were analyzed by refractive index measurement. It was found that n-Hexane-Propanol forms a minimum boiling azeotrope at 95 mole% Hexane at 65.8°C whereas Benzene-1-propanol form the same at 77.5 mole% benzene at 76°C. In the same year W. Shemilt and M. Waldichuck<sup>16</sup>

determined the vapour liquid equilibrium data at atmospheric pressure for the system (1-Butanol + Benzene) using a modified Gillespie still.<sup>26</sup> The astonishing feature of this measurement is that though azeotropes are found in (1-Butanol-Toluene) system, no azeotrope was obtained in (1-Butanol-Benzene) system. In the same year C.Y. Benzamin<sup>17</sup> used modified Gillespie still<sup>26</sup> to determine vapour liquid equilibria data for (cyclohexane-propanol) mixture. The mixture was found to form an azeotrope at 59.25 mole% cyclohexane at 68.6°C. In 1965, Isamu Nagata<sup>21</sup> used modified Gillespie still<sup>26</sup> to study vapour liquid equilibrium data for (Benzene-2-Propanol), (Cyclohexane-2-Propanol) and (2-Propanol-Methylcyclohexane) systems. All these mixtures were found to form azeotropes at compositions of 0.349, 0.360, 0.604 mole fraction 2-Propanol and at temperatures of 60.1°, 57.8°, 66.5°C respectively. In 1971, A. Khanna of our laboratory used the equilibrium still designed by Yerazunis, Flowright and Smola<sup>18</sup> to determine the isobaric vapour liquid equilibrium data for the system (Methylcyclohexane + Methylcyclohexanol) at a pressure of 760.00 mm. Hg. No azeotrope was found to be formed. The vapour and liquid samples were analysed by refractive index measurement.

In the present work the main aim is to study the non-ideality of systems having the same molecular size due to H and OH interaction. For this purpose the binary mixtures of (Methylcyclohexanol + n-heptane) and (Toluene + n-heptanol) have been studied. Since no vapour pressure data<sup>are</sup> available in the literature, vapour pressures have been measured over a wide range of pressure and temperature.

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## CHAPTER III

### APPARATUS AND EXPERIMENTAL PROCEDURE

#### Experimental Set-Up for the Equilibrium Apparatus:

The direct determination of vapour liquid equilibria involves separation of samples of liquid and vapour which are in true equilibrium with each other and determination of their concentration analytically. The vapour liquid equilibrium data can be obtained either at constant temperature or at constant pressure using the same set-up. In the present study the isobaric vapour liquid equilibrium data have been obtained for (i) (Methylcyclohexanol + n-Heptane) and (ii) (Toluene + n-Heptanol) over the whole composition range. The equilibrium still used for this work facilitates circulation of both vapour and liquid phases.

An equilibrium still is a vapour and liquid recirculation device which separates liquid and vapour phases in true equilibrium with each other. The design of the equilibrium still should be such that both temperature and pressure can be maintained constant quite accurately. Precaution is taken so that sampling of both vapour and liquid streams does not disturb the equilibrium. A still<sup>18</sup> which satisfies all these requirements has been used in the present work. A sketch of the separation chamber and reboiler is given in Figure 1(b) and 1(a) and a schematic description of the set-up is given in Figures 2 and 3.

The temperature measured in a boiling liquid or a vapour does not correspond to the true boiling point. This error due

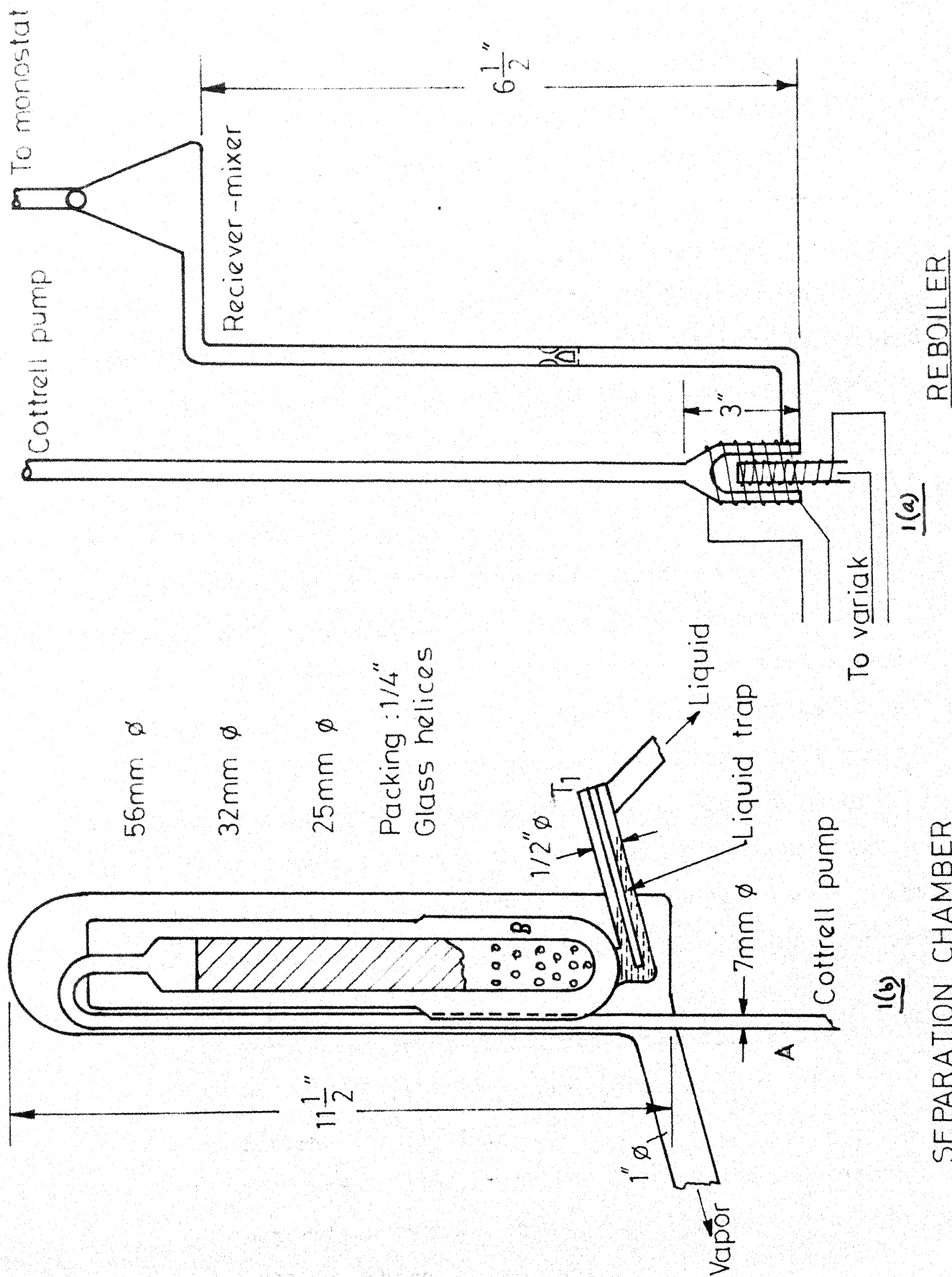


Fig.1(a)and (b).



to the effect of superheat is eliminated by means of a cottrell pump (A) and an equilibrium packed chamber (B). The cottrell pump is a small diameter tube through which slugs of liquid and vapour rise to the separation chamber (B). The vapour liquid mixture emerging from the cottrell tube is directed downwards through a short column (B) packed with glass beads and is disengaged only after the mixture has passed through the column in concurrent flow. The liquid streams past over a thermowell (T) and over-flows to the liquid sampling cell ( $S_1$ ). After separation the vapour passes upward around the packed column and then downward around the entire separation chamber providing a thermal barrier to the separation chamber. The vapor stream then passes into a condenser, the condensate from which flows to the vapour condensate sampling cell ( $S_2$ ). The overflows from the liquid and vapour condensate cells are combined in a receiver mixer (R) packed with glass beads before returning to the reboiler (E). The receiver mixer has been used to ensure thorough mixing between liquid and vapour overflows and to ensure that there is no concentration gradient between the two streams. The distinguishing features of the equilibrium still are:

- (i) The introduction of cottrell pump eliminates the possibility of measuring temperature of superheated liquid.
- (ii) The introduction of the short packed column in the separation chamber provides additional contact as well as enhances interfacial surface to bring

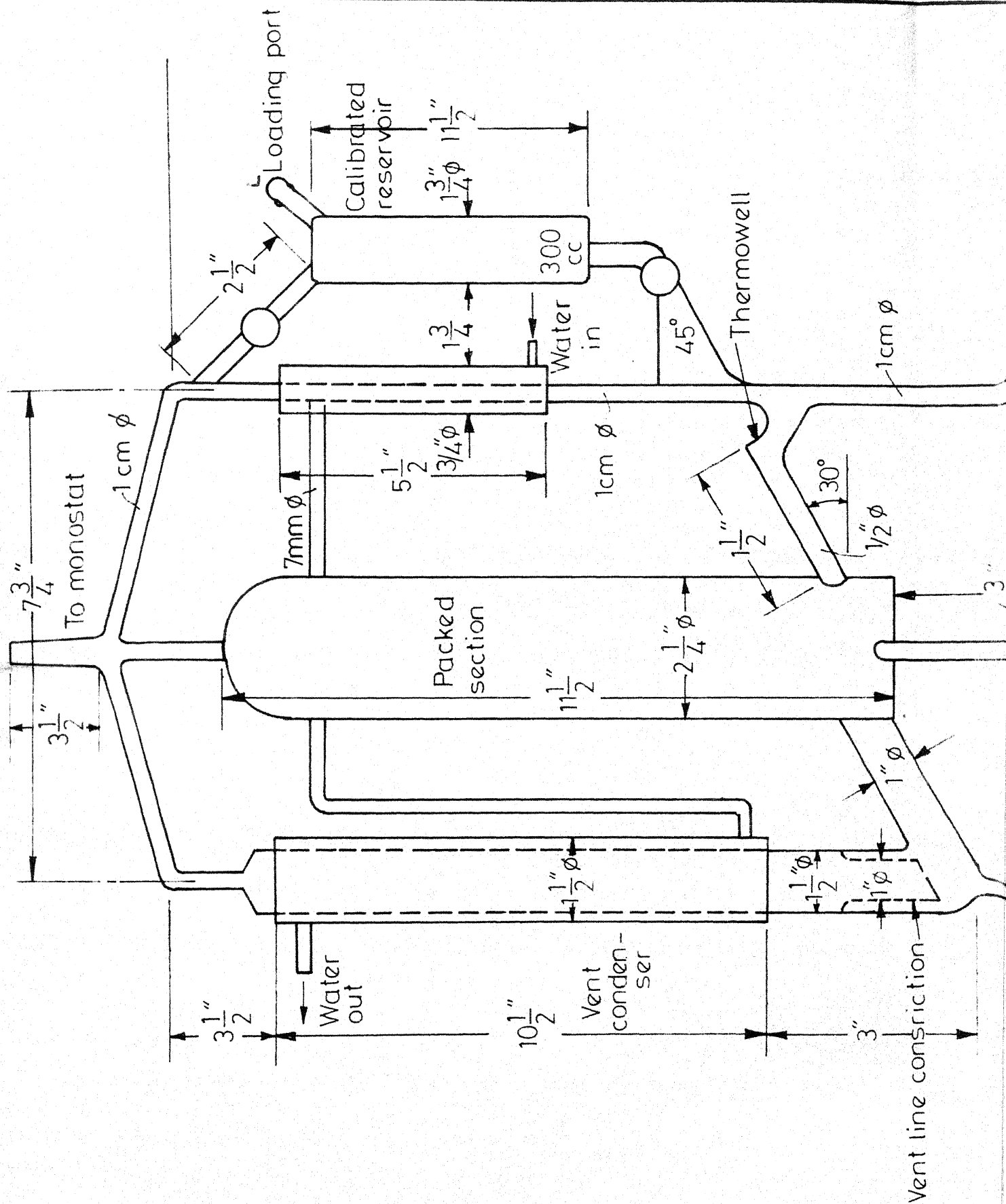


Figure 2

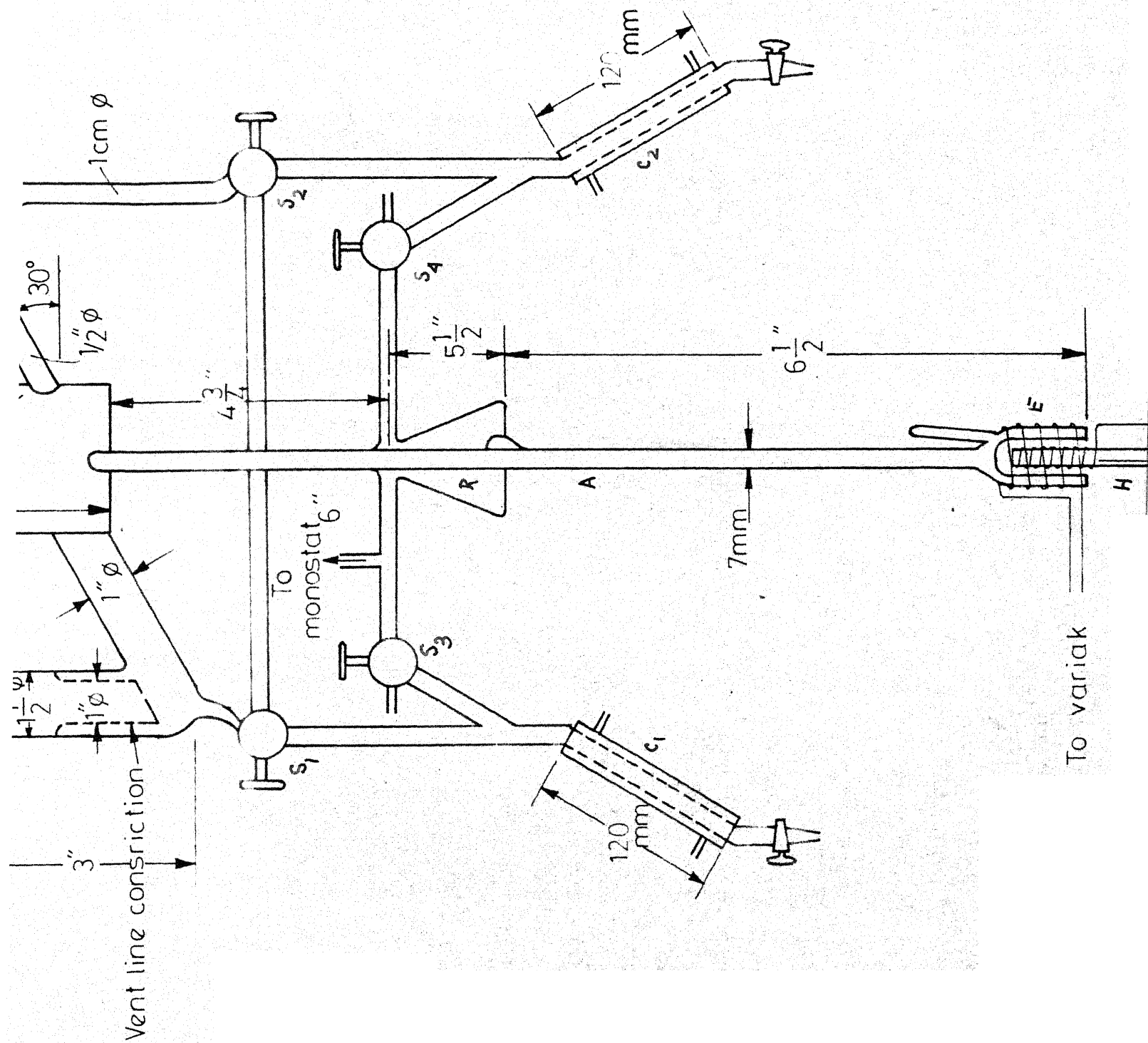
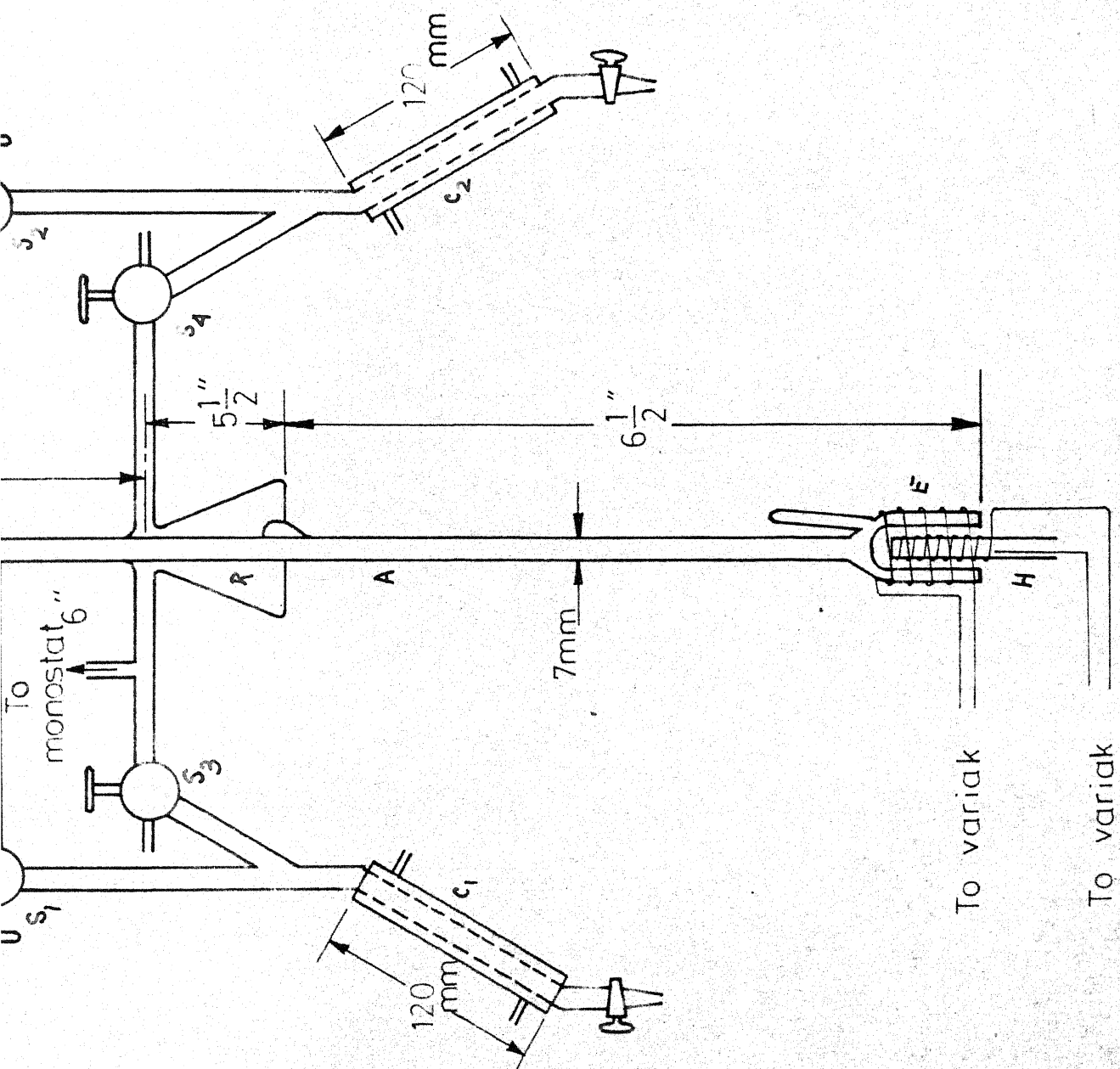


Figure 2

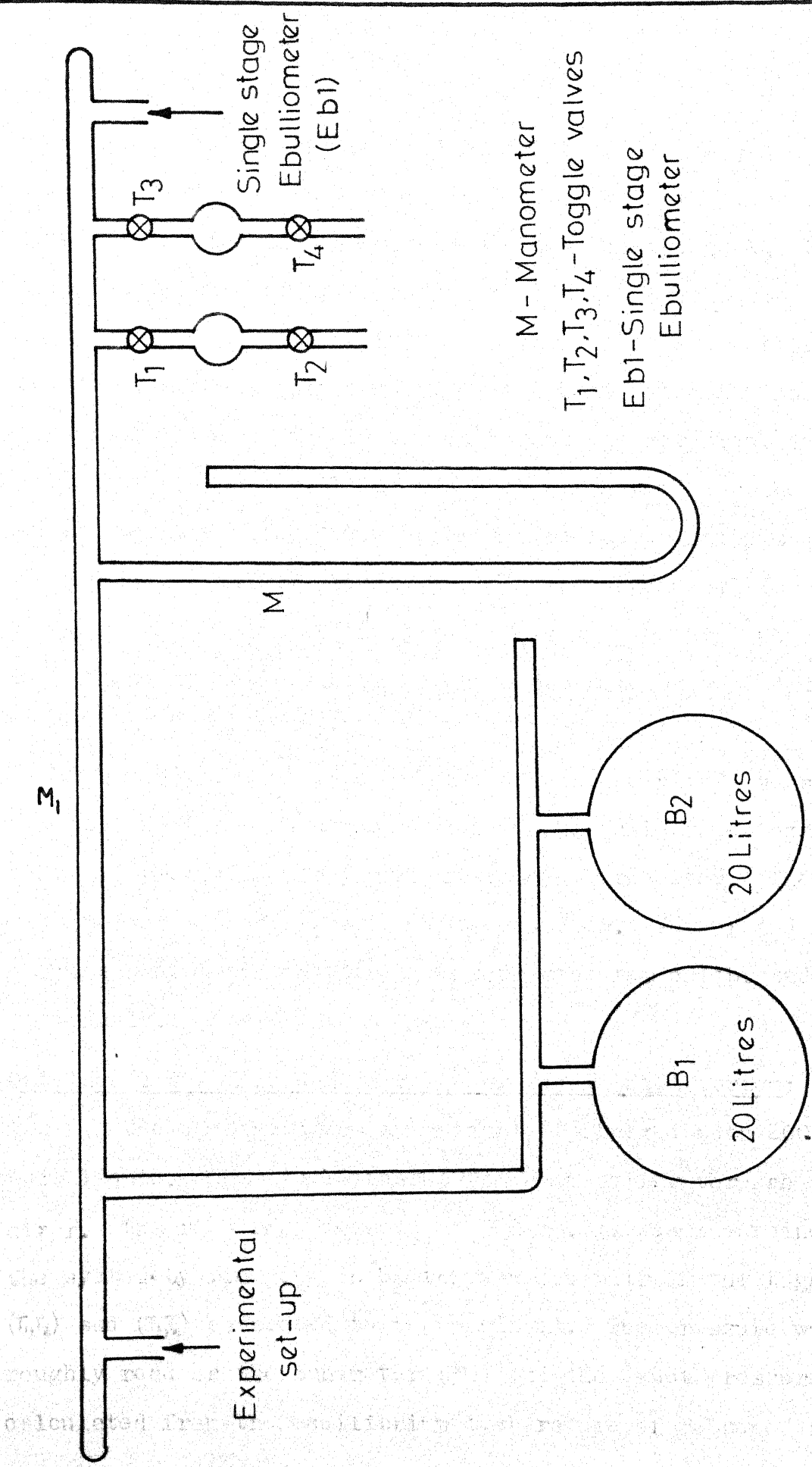


the two phases into a closer approach to equilibrium than that can be obtained in the cottrell tube itself.

- (iii) The use of vapour phase as a thermal barrier so that heat loss to the surroundings is reduced.
- (iv) The isolation of vapour and liquid sampling cells from the whole set-up.

The equilibrium still is connected to the manifold ( $M_1$ ) which, in turn, is connected to a single stage ebulliometer ( $E_{b1}$ ) a ballast ( $B_{12}$ ) and to the  $N_2$  cylinder and vacuum pump via two toggle valves. For rough measurement of pressure, a simple U-tube manometer is used. The single stage ebulliometer is used for accurate measurement of pressure in the system by boiling a standard liquid whose vapour pressure data are known. The ballast consists of two 25 litres flasks. The function of the ballast is to dampen the pressure-fluctuation in the system. The toggle valve provides quick action, their opening time being very small. This is useful to affect a very small change of pressure in the system. Requisite pressure in the system is maintained by bleeding  $N_2$  gas through the system.  $N_2$  is used to maintain an inert atmosphere in the system. To prevent the heat loss to the surroundings the equilibrium still is provided with a silvered double walled evacuated jacket. The reboiler, receiver mixer, cottrell pump and connecting tubes are insulated by glass wool.

During the operation of the experimental set-up following precautions are taken. Firstly level of the liquid in the



M - Manometer  
T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub> - Toggle valves  
Eb1 - Single stage Ebulliometer

Fig. 3 - Schematic diagram of the Experimental set-up.

reboiler is sufficient so that cottrell action is quite vigorous during the operation. To ensure this the liquid level in the reboiler should be at least at the neck. Secondly, circulation rate of both vapour and liquid streams play an important role in the operation. If the liquid to vapour circulation ratio is very high, then the heat added is inadequate. But on the other hand, if the same ratio is very low, superheating takes place. It is recommended that during the steady state operation liquid to vapour recirculation ratio should be nearly 2:1. Thirdly, liquid seal in the thermowell ensures complete separation of the liquid from the vapour. The liquid seal is maintained by having the thermo well at an inclination of  $30^\circ$  to the horizontal.

Equilibrium temperature has been accurately measured by means of a copper constantan thermocouple calibrated against a standard precision platinum resistance thermometer. The emf has been measured by a Precision Potentiometer. Vapour and liquid samples have been analyzed by a refractometer calibrated previously.

#### Outline of the Procedure for Vapour Liquid Equilibrium:

The apparatus was approximately charged with 200 ml. of pure liquid. The liquid passes to the reboiler through receiver mixer. The required pressure of 760 mm.Hg. was maintained in the system by bleeding in  $N_2$  through one pair of the toggle valves ( $T_1, T_2$ ) and ( $T_3, T_4$ ) connected to the manifold. The pressure was roughly read on the manometer (M) and the exact pressure was calculated from the equilibrium temperature of Benzene in the

ebulliometer ( $E_1$ ). The heaters on the equilibrium still (both external and finger heater) were turned on and throughout the experiment, the ballast ( $B_1, B_2$ ) was kept open to the system. Thus any amount of pressure fluctuation was dampened by the ballast. The finger heater ( $H$ ) is used to initiate the boiling of liquid in the reboiler. Initially because of expansion of  $N_2$  due to temperature rise in the system, there was a slight increase in pressure in the system. Pressure was then brought back to its original value by connecting the vacuum pump to the manifold by a pair of toggle valves ( $T_1, T_2$ ) and ( $T_3, T_4$ ). This kind of fluctuation was absent at or around the equilibrium state. The equilibrium still was operated under this condition for sufficient time so that equilibrium is ensured in the system. This is indicated by the constant temperature recorded by the thermocouple placed in thermo well ( $T_1$ ) and constant vapour to liquid circulation ratio over a length of time.

The sampling lines ( $S_1$ ) and ( $S_2$ ) were isolated from the equilibrium still during its normal operation. Before each sampling they were evacuated so that there is no liquid left from previous sampling and thus contamination of samples is avoided. After attainment of equilibrium in the system both liquid and vapour samples were taken in condensers ( $C_1$ ) and ( $C_2$ ) respectively. The vapour condensate and liquid sample cells were isolated from the system. The samples were cooled in the condensers to room temperature in order to avoid evaporation during the analysis. The three way stop cocks connected to the

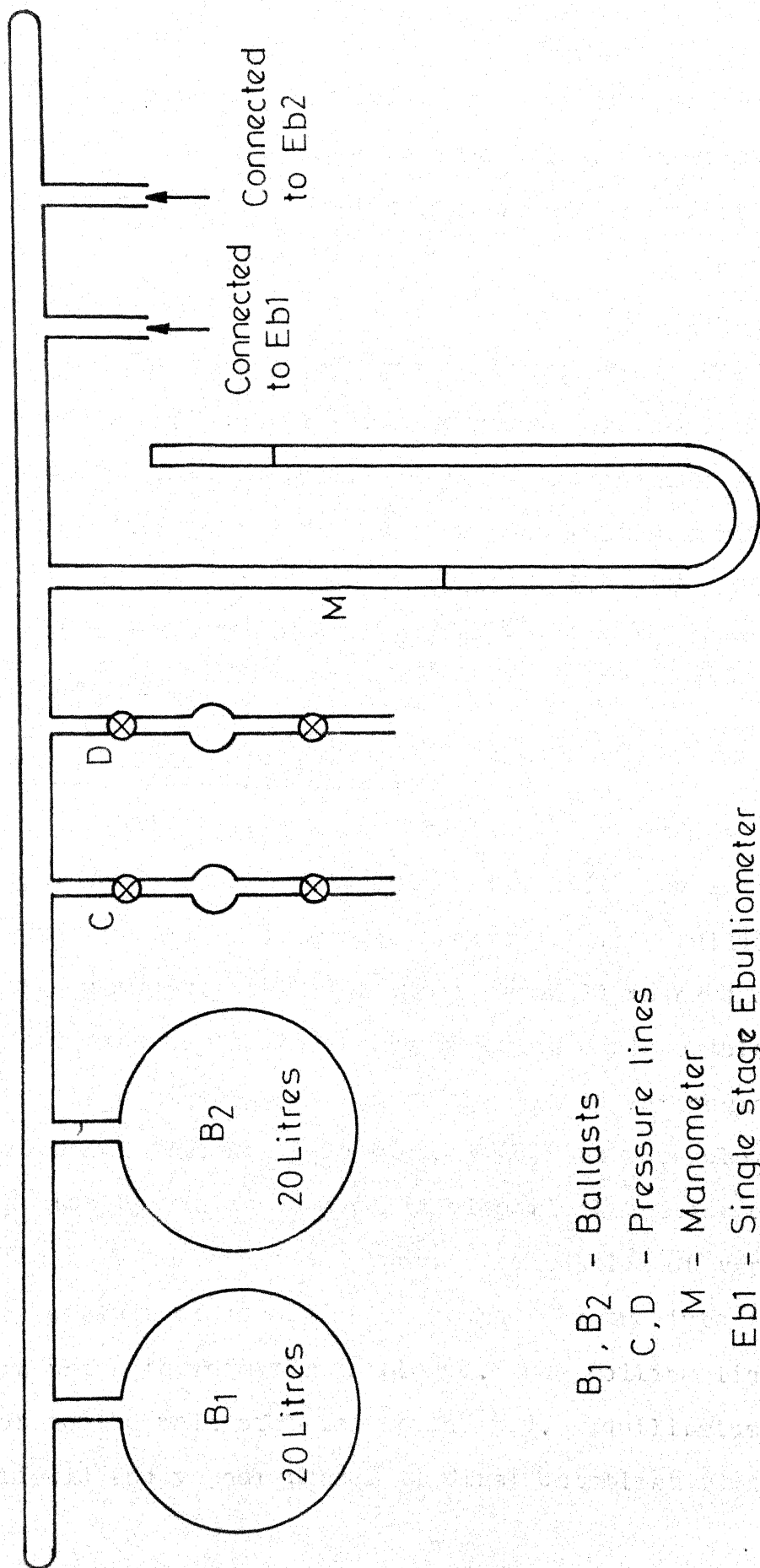


sampling lines ( $S_3$ ) and ( $S_4$ ) were opened to atmosphere and the samples were removed. They were subsequently analyzed for composition in a refractometer. This procedure was repeated atleast three times without further addition of fresh liquid. Then the requisite amount of the second pure component was added to the system through the loading port ( $L$ ) so that equilibrium was shifted to a new point. The same procedure was repeated for each equilibrium point. Approximately one half of the composition range could be studied before the reboiler( $E$ ) was needed to be emptied and the process was repeated starting with second pure component.

#### Experimental Set-Up and Procedure for Vapour Pressure Measurement:

Since the vapour pressure data for Methylcyclohexanol is not available in the literature. It is necessary to determine the vapour pressure data of methyl cyclohexanol.

The twin ebulliometric method is used for this purpose. The sketch of the set-up is given in Figure 4. The Eb1 contains the experimental liquid (i.e. Methylcyclohexanol) whereas Eb2 contains the reference liquid (i.e. Analar Toluene) for the accurate measurement of pressure. The lines (C) and (D) are used for evacuating the system and for flushing  $N_2$  in the system. These lines act as a means of adjusting the pressure in the system. The rough pressure in the system is indicated by the manometer (M). Both the experimental and reference liquids are allowed to boil simultaneously. The heat input to both the liquids is suitably adjusted. When the temperatures of both



B<sub>1</sub>, B<sub>2</sub> - Ballasts

C, D - Pressure lines

M - Manometer

Eb1 - Single stage Ebulliometer  
containing expl. liquid

Eb2 - Single stage Ebulliometer  
containing reference liquid

Fig. 4 - Vapor pressure set-up.

the liquids become steady, the temperatures are noted with the help of calibrated thermocouples. Since the vapour pressure data for Analar Toluene are known, it is possible to know the accurate pressure of the system. Thus the vapour pressure data for methylcyclohexanol is known.

The variac voltages (which controls the heat input) were kept from 30-36 volts for methylcyclohexanol and 20-24 volts for Analar Toluene. The readings of the boiling points were taken using different settings of variac voltages and it was found that they did not change significantly with different rate of heat input. This is a good proof that the experimental data are correct.

#### Single Stage Ebulliometer:

The single stage ebulliometers used in this work was originally designed by Swietoslowski.<sup>31</sup> The details of the ebulliometer are shown in Figure 5. The ebulliometer consists of a boiling chamber (B), a thermowell mounted on the chamber (A) connected to the boiler by means of a glass tube and opening to the condenser. 40 cc of the liquid was charged into the reboiler through the condenser (E) and the reboiler was externally heated by variac controlled electrical heating coil. The tube (D) acts as a cottrell pump. The bubbles of vapour carry with them slugs of liquid which spurt from the tube to the Thimble(T) in which thermometer is placed. The boiling liquid spurting on to the wall of T is superheated. Equilibrium between the liquid and vapour phases is first established on this thimble.

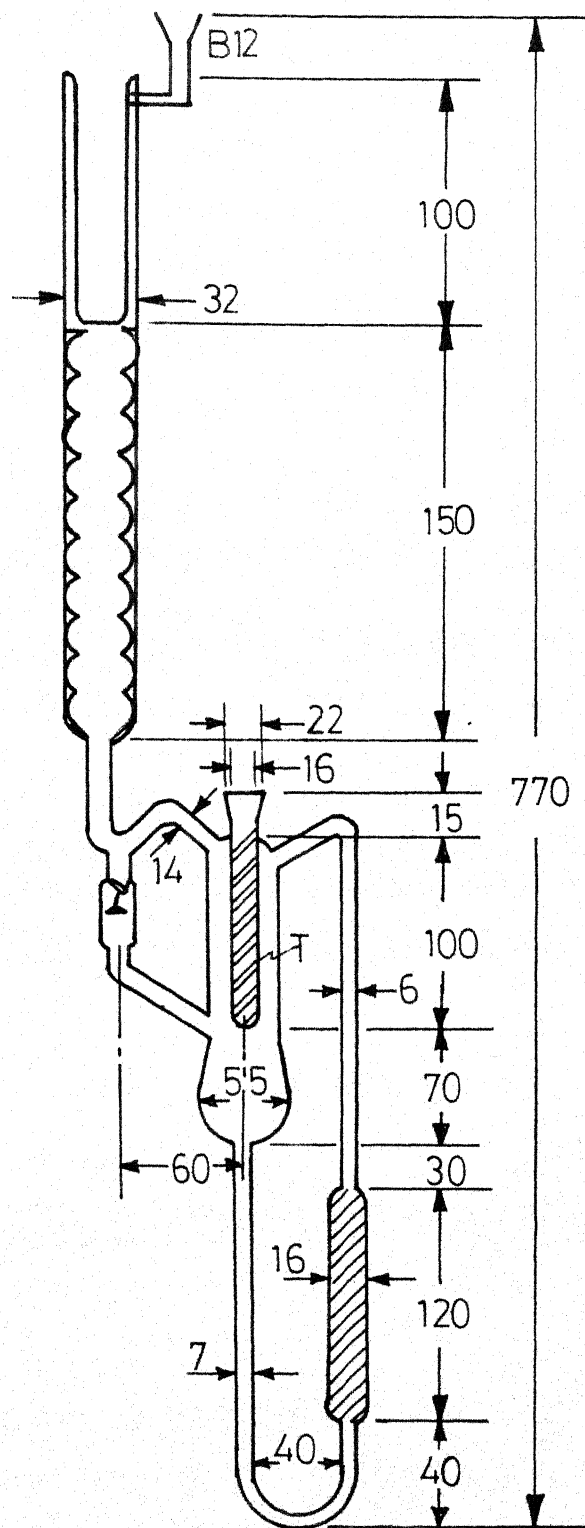


Fig. 5 -One stage Ebulliometer.

A small part of the falling superheated liquid vaporizes at the expense of its sensible heat. As a result, the temperature falls to the equilibrium value. Mercury is added to the thermometer well (A) to improve the heat transfer with the thermometer.

The vapours of the liquid are condensed in the condenser(E). The condensate from it flows through the drop counter (C) back into the boiling chamber (B). The drop counter is a straight tube with a broad orifice bent at right angles. A short rod ending in a hemisphere of diameter about 4 mm. is fused to its lower end. The drops form on the surface of this hemisphere. This type of drop counter is advantageous since a liquid seal is not formed and any pressure difference which may occur is rapidly ruled out.

The drop rate through the drop counter is never allowed to exceed a certain value and this is adjusted by controlling the heat input. For example, for water the drop rate should be between 8 to 25 drops per minute. For less than 8 drops/min. the heat addition is inadequate whereas for drop rate higher than 25 drops/min. superheating takes place. In order to prevent the heat loss to the surroundings, the boiling chamber, thermowell and the connecting tubes are properly insulated by glass wool.

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## CHAPTER IV

### SOURCE AND PURITY OF SAMPLES

The systems studied in the present investigation are the binary mixtures of (i) Methylcyclohexanol and n-Heptane and (ii) Toluene + n-Heptanol. Toluene was obtained as Analer grade from International Chemical Industries, Calcutta and n-Heptane from Kochlight Laboratories, England. n-Heptanol (BDH, LR) and Methyl Cyclohexanol (Riedel, LR) were distilled several times in a 5 foot-long distillation column packed with small glass tubings with a very high reflux ratio. The distillation set-up used for this purpose is described in Figure 6.

The liquid is charged in the flask (F) which is heated by a heating mantle. The heat supplied to the flask is adjusted depending on the Boiling point. of the liquid to be distilled. The vapour fractionates through the packed column (G) and condensed vapour is collected in the receiver flask (H). To prevent heat loss to the surroundings column is provided with a silvered double walled evacuated jacket. The column is operated under vacuum for more efficient distillation and to avoid decomposition of the compounds. During distillation the column has to be run with high reflux ratio. This is obtained by opening the stop cock (I) for 1 min. and closing it for five minutes.

For distillation of Methyl cyclohexanol the pressure in the line was maintained between 11-18 mm. and the variac voltage was kept at 128 volts. The distillation was carried out five times. N-heptanol was distilled twice. The variac

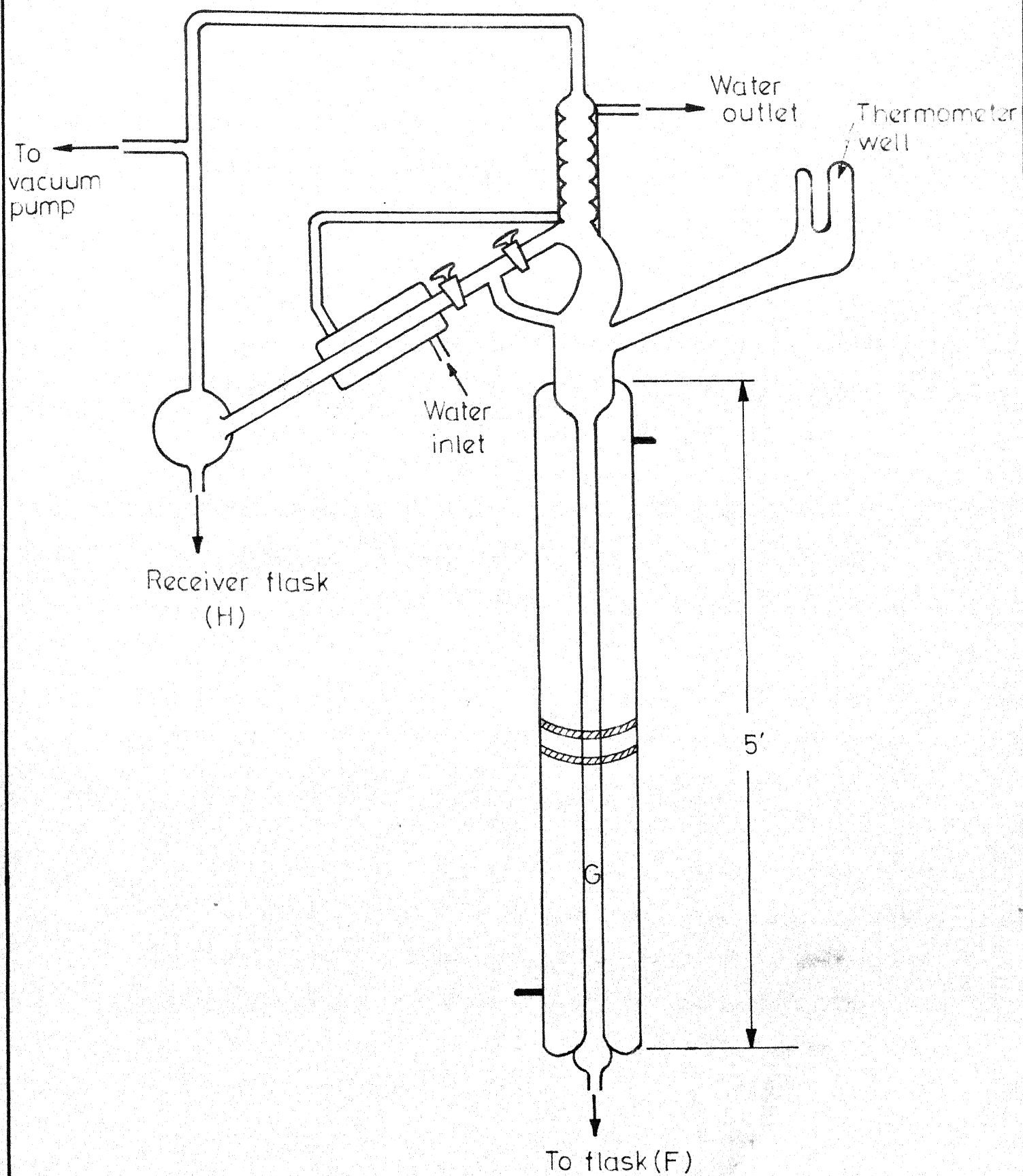


Fig 6 - Distillation set-up.

voltage was kept at 125 volts and the pressure in the line was maintained at 16-19 mm. The compounds were then subjected to ebulliometric test for purity on a differential ebulliometer.

The diagram of a differential ebulliometer is shown in Figure 7.

The differential ebulliometer essentially consists of two single stage ebulliometers as designed by Swietoslawski<sup>31</sup> connected to each other. The siphon (S) in the head (B) is wound with heating wire or fitted with a microburner, with which the bend can be heated. The ebulliometer is filled with the liquid whose purity is to be checked. The reboiler is heated externally by means of a variac controlled coil heater. When the vapours rise into the head (B) and the condensate forming in the condenser (C<sub>1</sub>) flows through the drop counter into the siphon(S) the microburner connected to the siphon (S) is put on and the amount of heat input to it is regulated so that the number of drops in both drop counters ( P<sub>1</sub> and P<sub>2</sub>) is the same. When the temperatures in both wells (T<sub>1</sub>) and (T<sub>2</sub>) become constant, the temperature as recorded by both the thermo wells are noted. The thermo well (T<sub>1</sub>) gives the boiling temperature whereas the thermo well (T<sub>2</sub>) gives the condensation temperature. The difference between these two temperatures (  $\Delta t$ ) is an indication of the purity of the substance.

The results of the purity analysis are given in Table I.



TABLE IPURITY ANALYSIS

Compound	Boiling point (°C)	Condensation Temperature (°C)	Difference (°C)
n-Heptane (AR)	97.38	97.36	0.02
Methyl Cyclo- hexanol	170.64	170.51	0.13
Toluene (AR)	110.63	110.61	0.02
n-Heptanol	174.07	173.97	0.10

## CHAPTER V

### EXPERIMENTAL RESULTS

Experimental results of the systems Methylcyclohexanol-n-Heptane and Toluene-Heptanol are being presented in Tables II and IV respectively in the T-x-y format. These results have been smoothened by regression analysis and the smoothened data have been presented in Tables III and V. T-x-y data for both the systems as mentioned earlier have been plotted in Figures 8 and 10 and y-x data in Figures 9 and 11 respectively. Experimental vapour pressure data for Methylcyclohexanol have been given in Table VI and have been correlated for Martin equation satisfactorily. The Martin's equation has the following form:

$$\log P = A + B/T + CT + DT^2 + ET^3 + F \log(G-T) \quad (V.1)$$

The constants A,B,C,D,E,F and G have been found by regression analysis, and have been tabulated in Table VI. Log P has been plotted against  $\frac{1}{T}$  (t in °C) using different values of C in Antoine's equation and has been shown in Figure 12. The activity coefficients of the individual components in the mixture have been calculated and given in Tables VII and VIII.

TABLE II

EXPERIMENTAL DATA: METHYLCYCLOHEXANOL(1)+n-HEPTANE(2) AT  
PRESSURE OF 760 mm Hg.

<u>Temperature(°C)</u>	<u>Liquid Composition (<math>x_1</math>)</u>	<u>Vap. Composition (<math>y_1</math>)</u>
99.619	0.0688	0.0194
100.023	0.1074	0.0345
101.374	0.1559	0.0569
102.124	0.2139	0.0748
104.368	0.2783	0.0807
105.008	0.3403	0.1015
106.946	0.4315	0.1118
108.157	0.4992	0.1177
109.472	0.5472	0.1251
112.117	0.6180	0.1485
115.022	0.6849	0.1704
120.018	0.7741	0.2110
123.542	0.8416	0.2412
133.619	0.8801	0.3542
143.523	0.9264	0.4871
146.924	0.9382	0.5472
154.823	0.9534	0.7204
161.767	0.9847	0.8861

TABLE IIISMOOTHENED DATA: METHYL CYCLOHEXANOL(1)+n-HEPTANE(2)AT 760.00 mm.Hg.

<u>Temperature (°C)</u>	<u>Liquid Composition (<math>x_1</math>)</u>	<u>Vapour Composition (<math>y_1</math>)</u>
98.93	0.0688	0.0207
99.47	0.1074	0.0367
100.63	0.1559	0.0551
102.37	0.2139	0.0718
104.37	0.2783	0.0843
106.07	0.3403	0.0934
107.91	0.4315	0.1083
108.86	0.4992	0.1223
109.49	0.5472	0.1330
110.76	0.6180	0.1480
112.95	0.6849	0.1617
118.92	0.7741	0.1951
127.17	0.8416	0.2667
133.88	0.8801	0.3482
144.38	0.9264	0.5126
147.53	0.9382	0.5702
151.91	0.9534	0.6559
162.13	0.9847	0.8810

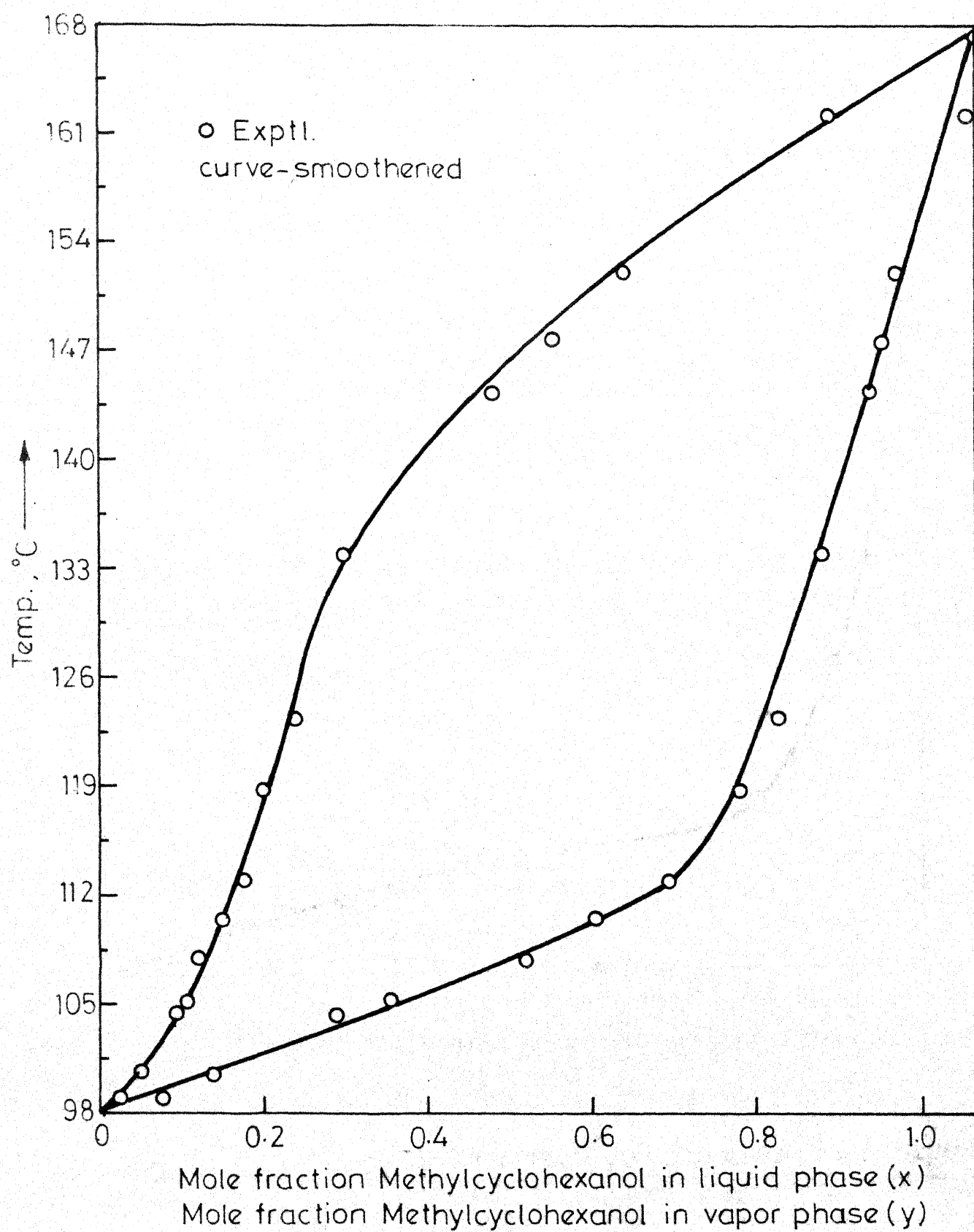


Fig.8 - (T-x-y) diagram for (Methycyclohexanol + n Heptane<sup>2</sup>).

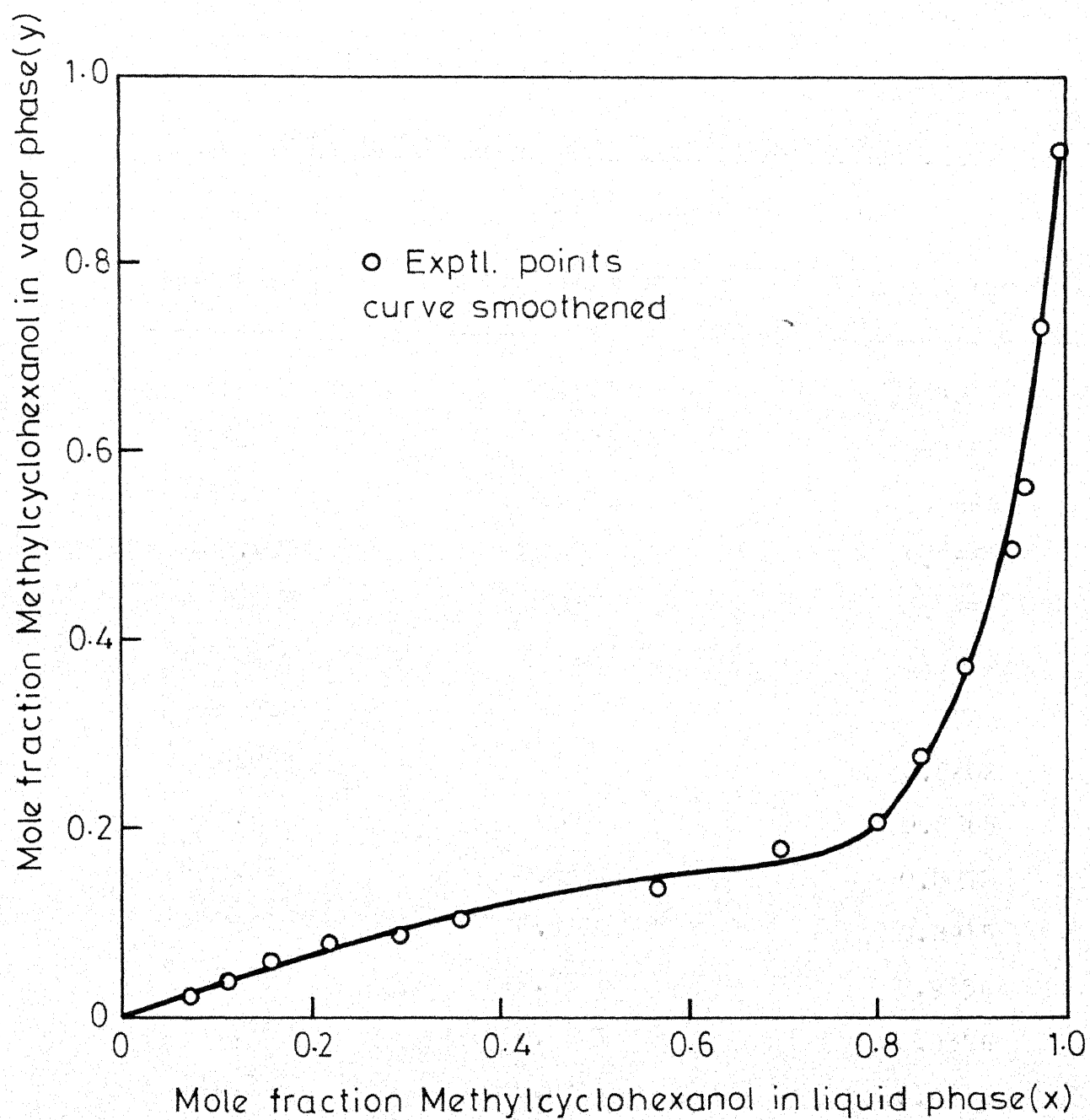


Fig. 9 - (y-x) diagram for (Methylcyclohexanol<sup>1</sup> + n-Heptane<sup>2</sup>).

TABLE IV

EXPERIMENTAL DATA: TOLUENE(1)+n-HEPTANOL(2) AT760 mm. Hg.

<u>Temperature</u> (°C)	<u>Liquid Composition</u> ( $x_1$ )	<u>Vapour Composition</u> ( $y_1$ )
165.804	0.0641	0.1251
156.249	0.2039	0.3582
150.247	0.2613	0.4886
143.685	0.3264	0.5861
140.306	0.3552	0.6651
133.619	0.4202	0.7529
129.569	0.4561	0.7792
126.883	0.5204	0.8202
122.043	0.5822	0.8565
119.328	0.6516	0.8772
117.107	0.7057	0.8915
115.385	0.7506	0.9134
114.164	0.7871	0.9376
112.244	0.8321	0.9414
111.124	0.8803	0.9574

TABLE VSMOOTHENED DATA: TOLUENE(1) + n-HEPTANOL (2) AT760 mm. Hg.

<u>Temperature</u> <u>(°C)</u>	<u>Liquid Composition</u> <u>(<math>x_1</math>)</u>	<u>Vapor Composition</u> <u>(<math>y_1</math>)</u>
167.94	0.0641	0.1323
155.13	0.2039	0.3959
149.43	0.2613	0.4969
143.04	0.3264	0.6011
140.29	0.3552	0.6427
134.41	0.4202	0.7258
131.39	0.4561	0.7647
126.47	0.5204	0.8222
122.42	0.5822	0.8631
118.69	0.6516	0.8943
116.38	0.7057	0.9101
114.85	0.7506	0.9194
113.83	0.7871	0.9258
112.83	0.8321	0.9336
112.02	0.8803	0.9446



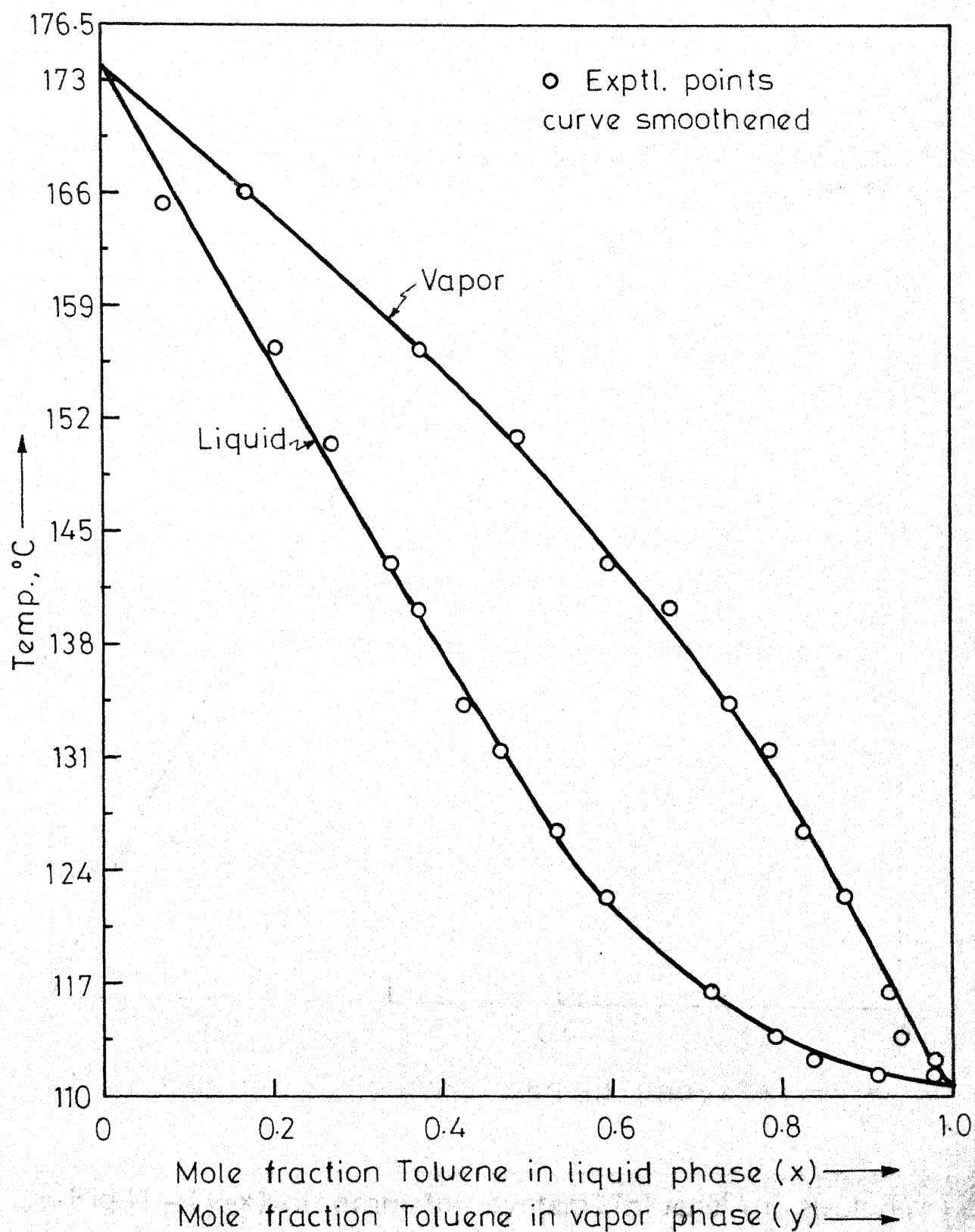


Fig.10 - (T-x-y) diagram for Toluene + Heptanol<sup>2)</sup>

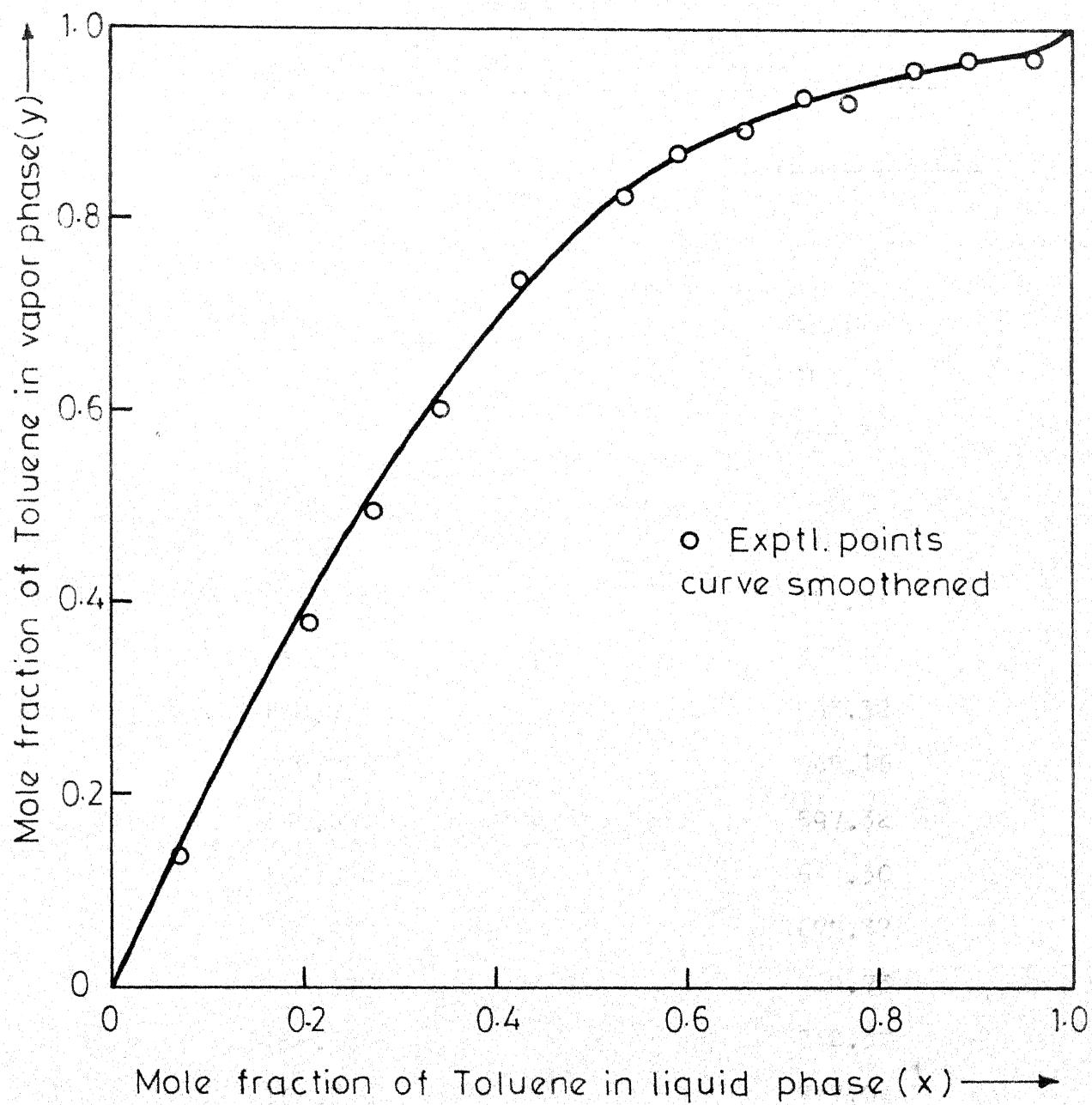


Fig.11 - (y-x) diagram for system(Toluene<sup>1</sup> + n-Heptanol<sup>2</sup>).

TABLE VIVAPOUR PRESSURE DATA FOR METHYLCYCLOHEXANOL

<u>Temperature (°C)</u>	<u>Pressure (mm.Hg.)</u>
130.270	236.82
135.011	277.51
137.949	322.89
142.432	353.56
145.940	395.25
148.808	435.12
151.264	466.39
154.168	510.81
158.380	556.67
158.777	563.32
158.895	565.16
159.584	597.32
162.080	647.30
164.277	677.32
166.077	729.73
168.186	742.37
168.596	747.04
170.155	795.07

The constants of the Martin's equation are:

$$\begin{aligned} A &= .77898216 & B &= 2368.510 & C &= .0227261 \\ D &= .72965495E-04 & E &= -0.14531388E-06 & F &= -8.113654 \\ G &= 602.15000 \end{aligned}$$

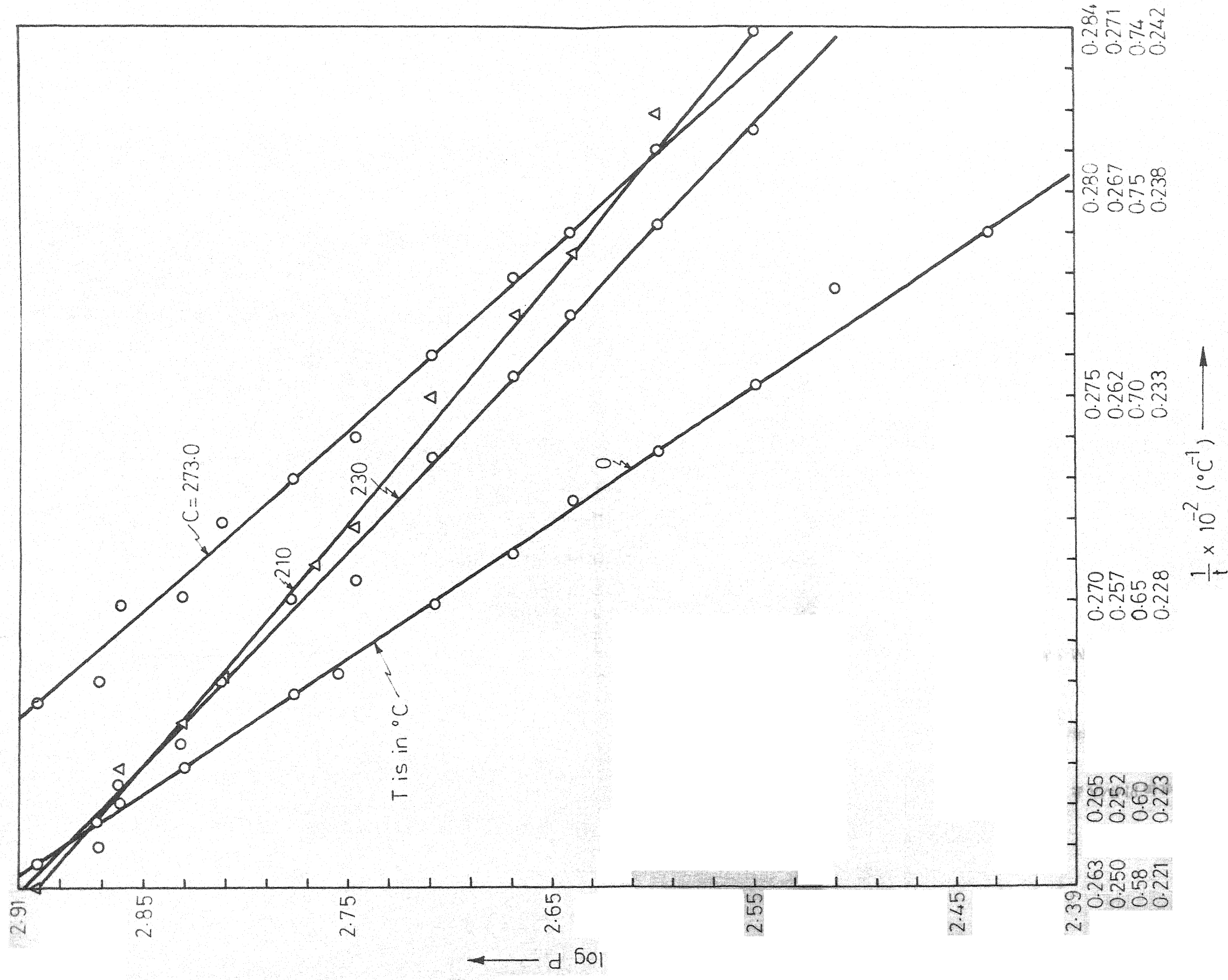


Fig.12 - Plot of log P vs.  $\frac{1}{T}$  taking different values of C in Antoine's eqn.

The activity coefficients have been calculated from vapour liquid equilibrium data by the equations (V-2) and (V-3)

$$\gamma_1 = \frac{P y_1}{P_1^0 x_1} \exp \frac{(B_{11} - v_1^{OL}) (P - P_1^0) + (2B_{12} - B_{11} - B_{22}) y_2^2 P}{RT} \quad (V.2)$$

$$\gamma_2 = \frac{P y_2}{P_2^0 x_2} \exp \frac{(B_{22} - v_2^{OL}) (P - P_2^0) + (2B_{12} - B_{11} - B_{22}) y_1^2 P}{RT} \quad (V.3)$$

where  $P_1^0$ ,  $P_2^0$  represent the vapour pressure data,  $B$  the virial coefficient,  $v$  the molar volume.  $\ln \gamma_1$  and  $\ln \gamma_2$  for both the systems have been presented in Table VII and VIII respectively and have been plotted against composition in Figures 13 and 14.

TABLE VIIMETHYLCYCLOHEXANOL(1) + n-HEPTANE(2) AT 760 mm.Hg.

(With smoothened data)

Liquid Composition ( $x_1$ )	Activity Co-efficient of compound ( $\gamma_1$ )	Activity Co-efficient of compound ( $\gamma_2$ )	$\ln \gamma_1$	$\ln \gamma_2$
0.0688	2.2359	1.0371	0.8046	0.0364
0.1074	2.4964	1.0485	0.9148	0.0473
0.1559	2.4890	1.0535	0.9119	0.0521
0.2139	2.2376	1.0599	0.8054	0.0581
0.2783	1.8960	1.0794	0.6397	0.0764
0.3403	1.6286	1.1176	0.4877	0.1112
0.4315	1.4059	1.2156	0.3407	0.1952
0.4992	1.3322	1.3252	0.2869	0.2816
0.5472	1.2960	1.4245	0.2593	0.3538
0.6180	1.2274	1.6062	0.2049	0.4739
0.6849	1.1305	1.8125	0.1227	0.5947
0.7741	1.0045	2.0953	0.0045	0.7397
0.8416	0.9849	2.2426	-0.0152	0.8077
0.8801	1.0093	2.2667	0.0092	0.8183
0.9264	1.0468	2.2124	0.0457	0.7941
0.9382	1.0538	2.1805	0.0524	0.7796
0.9534	1.0590	2.1243	0.0573	0.7534
0.9847	1.0533	1.8489	0.0519	0.6146

TABLE VIII

TOLUENE (1) + n-HEPTANOL (2) AT 760 mm.Hg.

Liquid Composition ( $x_1$ )	Activity Co-efficient of compound ( $\gamma_1$ )	Activity co-efficient of compound ( $\gamma_2$ )	$\ln \gamma_1$	$\ln \gamma_2$
0.0641	0.5508	1.0176	-0.5964	0.0175
0.2039	0.6727	1.2206	-0.3965	0.1993
0.2613	0.7439	1.3139	-0.2958	0.2730
0.3264	0.8291	1.4140	-0.1874	0.3464
0.3552	0.8667	1.4549	-0.1431	0.3749
0.4202	0.9476	1.5316	-0.0538	0.4263
0.4561	0.9880	1.5663	-0.0121	0.4487
0.5204	0.0490	1.6190	-0.0478	0.4818
0.5822	1.0887	1.6790	0.0850	0.5182
0.6516	1.1086	1.8097	0.1031	0.5932
0.7057	1.1061	2.0066	0.1009	0.6964
0.7506	1.0937	2.2652	0.0896	0.8177
0.7871	1.0791	2.5520	0.0761	0.9369
0.8321	1.0572	3.0237	0.0556	1.1065
0.8803	1.0333	3.6657	0.0327	1.2990

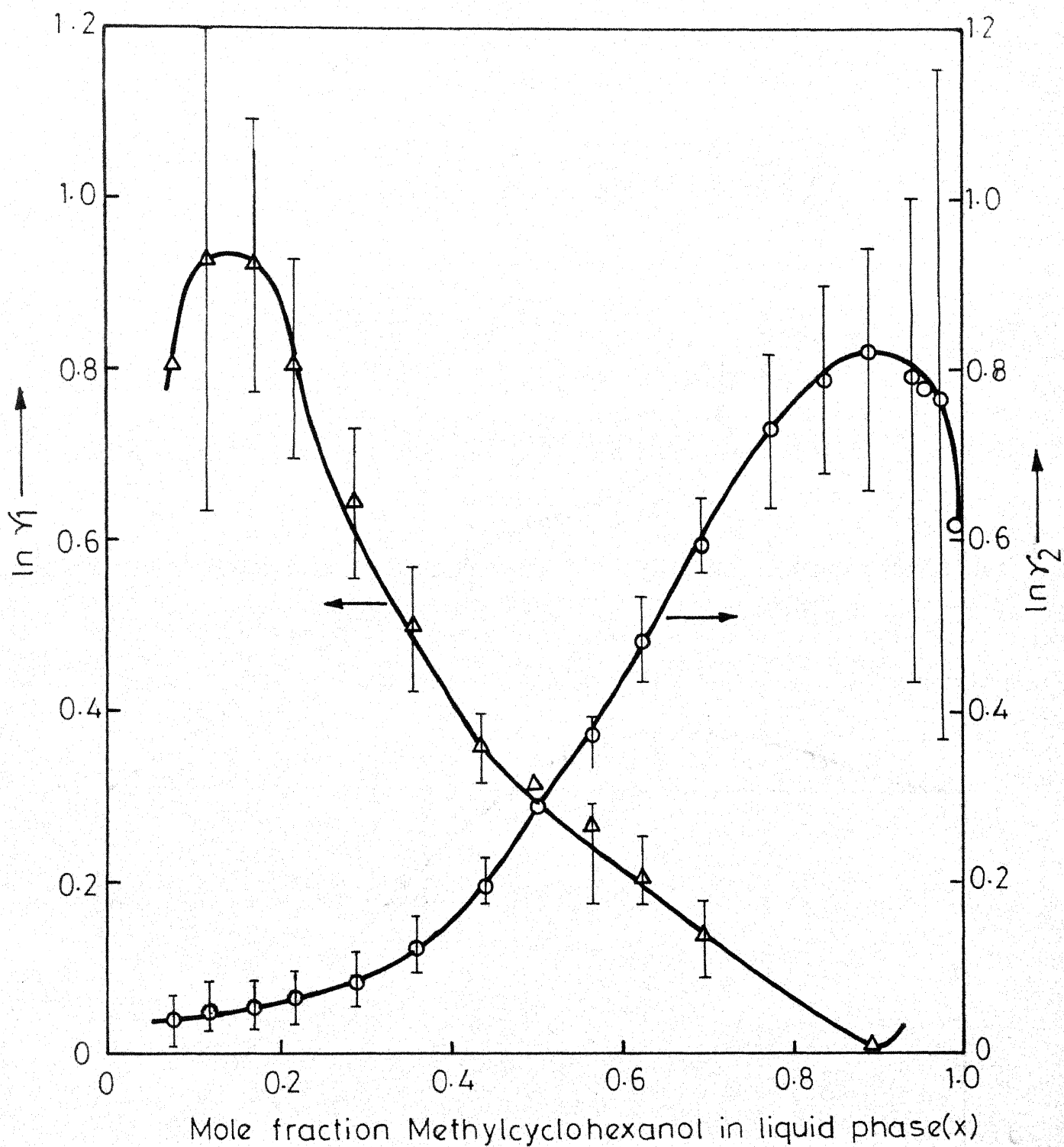


Fig.13 -  $\ln \gamma_1$  vs.  $x$  and  $\ln \gamma_2$  vs.  $x$  for (Methylcyclohexanol<sup>1</sup> + n-Heptane<sup>2</sup>).

(Verticle lines indicate error at each exptl. point)



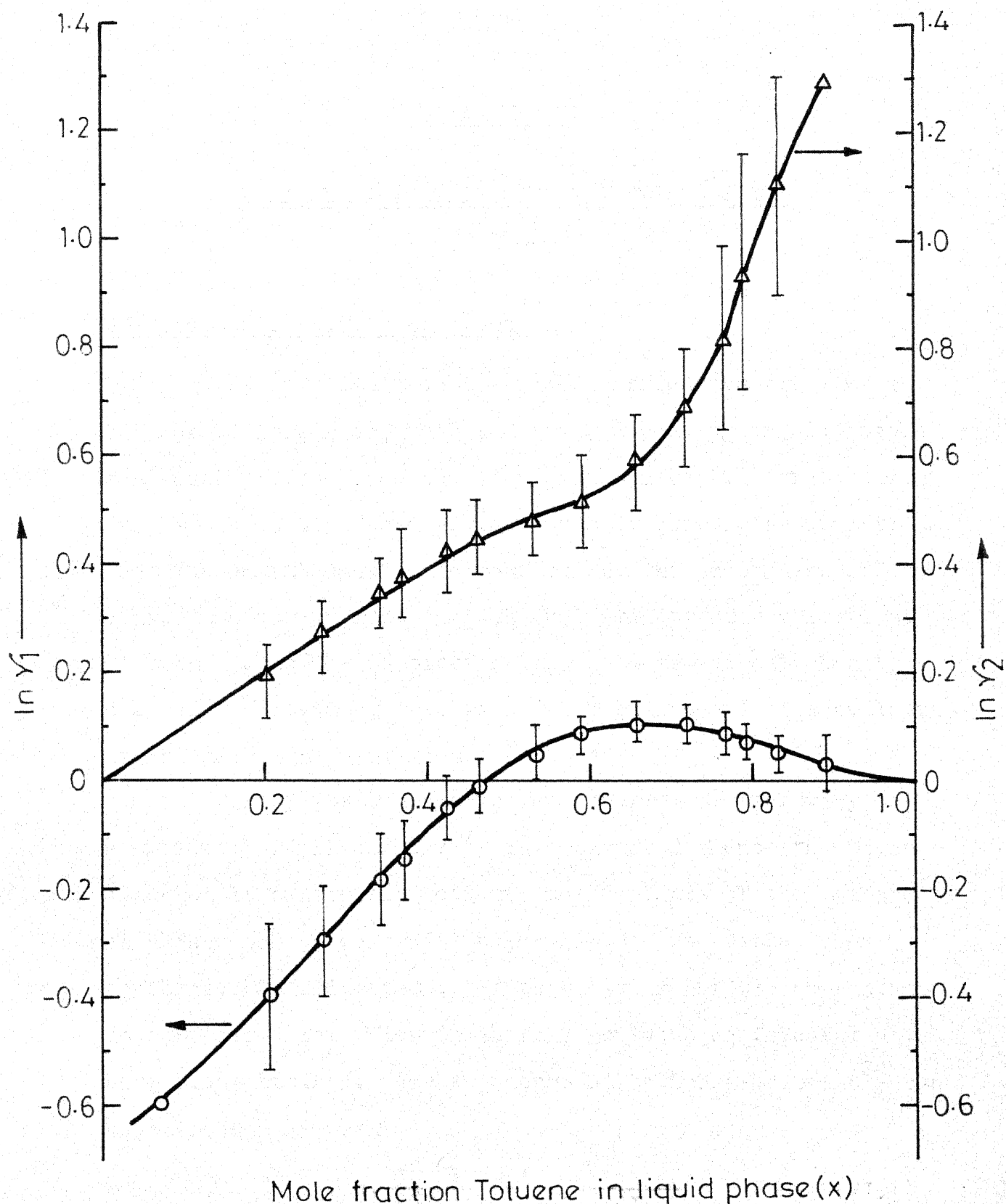


Fig.14 -  $\ln \gamma_1$  vs.  $x$  and  $\ln \gamma_2$  vs.  $x$  for (Toluene + n-Heptanol)  
 (Vertical lines indicate error at each exptl. point)

## CHAPTER VI

### THERMODYNAMIC CONSISTENCY TEST AND ERROR ANALYSIS

#### Thermodynamic Consistency Test:

Vapour liquid equilibrium measurements are always subject to larger or smaller errors, depending on the instrument used and the accuracy of the measurement. Large random errors are easily found as they usually show up as deviations from the smooth curve. In some cases, the smoothness of the curve is not a guarantee of the reliability of the results. In such a case the consistency of the measured data can be checked by comparing them with the requirements of some thermodynamically exact relation.

The Gibbs Duhem equation interrelates activity coefficients of all components in a mixture. Hence the thermodynamically consistent activity coefficients of the components as a function of composition should obey the Gibbs Duhem equation. To illustrate, a binary mixture of two components is considered for which isothermal activity coefficient data have been obtained. For this case Gibbs Duhem equation<sup>29</sup> can be written as

$$x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2} \quad (\text{VI.1})$$

Plots of  $\ln \gamma_1$  vs.  $x_1$  and  $\ln \gamma_2$  vs.  $x_2$  are prepared and slopes of the corresponding curves are measured at different points. These slopes are then substituted in equation (VI.1) at various

compositions to check whether equation (VI.1) is satisfied. If equation (VI.1) is satisfied conclusion can be reached that data are thermodynamically consistent. Although the above method is quite convenient, it is of little practical value since it is difficult to measure slopes with sufficient accuracy. So it provides a poor method for testing the thermodynamic consistency of the data. However the integral test as was proposed by Redlich and Kister<sup>29</sup> and also by Herington<sup>29</sup> overcomes the above mentioned difficulty. In the integral test the molar excess free energy of mixing is written as:

$$\begin{aligned} \frac{g^E}{RT} &= x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \\ \therefore \left. \frac{d(g^E/RT)}{dx_1} \right|_{T,P} &= x_1 \frac{d \ln \gamma_1}{dx_1} + \ln \gamma_1 + x_2 \frac{d \ln \gamma_2}{dx_1} \\ &\quad + \ln \gamma_2 \frac{dx_2}{dx_1} \end{aligned} \quad (VI.2)$$

Since  $dx_2 = -dx_1$  and according to Gibbs Duhem equation by proper rearrangement of equation (VI.2), we obtain

$$\left. \frac{d(g^E/RT)}{dx_1} \right|_{T,P} = \ln \frac{\gamma_1}{\gamma_2} \quad (VI.3)$$

Integrating with respect to  $x_1$  over the whole composition range,

$$\begin{aligned} \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 &= \left( \frac{g^E}{RT} \right)_{x_1=1} - \left( \frac{g^E}{RT} \right)_{x_1=0} \\ &= 0 - 0 = 0 \end{aligned}$$

Therefore  $\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0$

i.e. if the logarithm of  $\frac{\gamma_1}{\gamma_2}$  calculated from the measured data, is plotted against  $x_1$  on the graph, the total area under the curve must be equal to zero.

Herington generalized this procedure to include isobaric data. According to him, the areas A and B need not be same and the value of the integral, which is the algebraic sum of these areas, will be equal to I. That is,

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx = I$$

If the sum of the magnitudes of areas A and B (without regard to sign) is denoted by  $\Sigma$ , the percentage deviation D is expressed by the equation

$$D = \frac{100 |I|}{\Sigma}, \quad |I| \text{ being the absolute value of } I.$$

This percentage deviation D is compared with another value J, which is a function of the overall range of boiling points of the system at the given pressure and the lowest measured boiling temperature in °K ( $T_{\min}$ )

$$J = \frac{150 |P|}{T_{\min}}$$

Herington states that if  $(D-J) < 10$ , the data can be considered to be thermodynamically consistent.

In the present work Herington's area test<sup>29</sup> has been used to check the thermodynamic consistency of the experimental

data. For this purpose  $\ln \frac{\gamma_1}{\gamma_2}$  vs.  $x$  has been plotted for both the systems (Methylcyclohexanol + n-heptane) and (Toluene + n-Heptanol). These results are put down in Tables IX and X.

Figure 15 shows the plot of  $\ln \frac{\gamma_1}{\gamma_2}$  vs  $x_1$  for the system (Methylcyclohexanol + n-heptane). The area above x-axis  $I_1 = 27.06 \times 10^{-2}$  units of area (found by graphical integration) The area below x-axis  $I_2 = 26.81 \times 10^{-2}$  units of area.

$$I = I_1 - I_2 = .25 \times 10^{-2} \text{ units of area}$$

$$\Sigma = I_1 + I_2 = .5387 \times 10^{-2} \text{ units of area}$$

The difference between the boiling points of 1 and 2,  
 $P = 69.43^\circ\text{C}$ ,  $T_{\min} = 371.42^\circ\text{K}$

$$\therefore D = \frac{100 \times .0025}{.5387} = 0.464$$

$$J = \frac{150 \times 69.43}{371.42} = 28.0$$

Since  $D \ll J$ , Herington's criteria for thermodynamic consistency is satisfied. It can be concluded that the data are thermodynamically consistent.

Figure 16 shows the plot of  $\ln \frac{\gamma_1}{\gamma_2}$  vs.  $x_1$  for the system (Toluene + n-Heptanol) only there is area below x-axis, i.e.  $I_2$  exists where as  $I_1 = 0$ .

$$\therefore I = \Sigma$$

$$\text{Hence } D = 100$$

The difference between the boiling points of toluene and n-heptanol  $P = 63^\circ\text{C}$ ,  $T_{\min} = 333.8^\circ\text{K}$

TABLE IXMETHYLCYCLOHEXANOL(1)+n-HEPTANE AT 760 mm.Hg.

Liquid Composition ( $x_1$ )	$\ln \frac{\gamma_1}{\gamma_2}$
0.0688	0.7682
0.1074	0.8675
0.1559	0.8598
0.2139	0.7473
0.2783	0.5633
0.3403	0.3765
0.4315	0.1455
0.4992	0.0053
0.5472	-0.0946
0.6180	-0.2689
0.6849	-0.4720
0.7741	-0.7352
0.8416	-0.8229
0.8801	-0.8091
0.9264	-0.7484
0.9382	-0.7271
0.9534	-0.6961
0.9847	-0.5626

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TABLE XTOLUENE(1) + n-HEPTANOL(2) AT 760 mm.Hg.

Liquid Composition ( $x_1$ )	$\ln \frac{\gamma_1}{\gamma_2}$
0.0641	-0.6139
0.2039	-0.5958
0.2613	-0.5689
0.3264	-0.5338
0.3552	-0.5180
0.4202	-0.4801
0.4561	-0.4608
0.5204	-0.4350
0.5822	-0.4332
0.6516	-0.4901
0.7057	-0.5956
0.7506	-0.7280
0.7871	-0.8608
0.8321	-1.0509
0.8803	-1.2663

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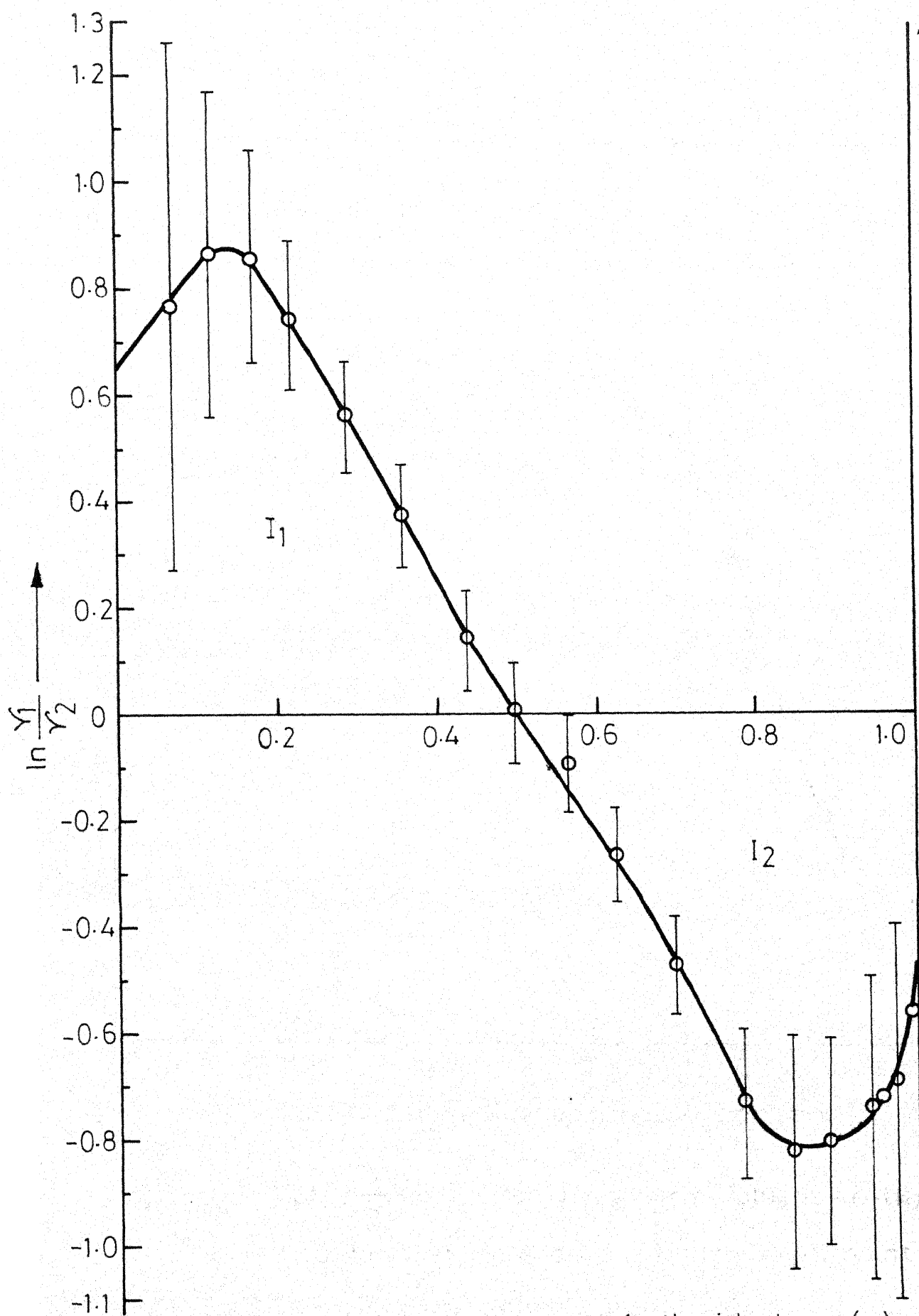


Fig.15 - Plot of  $\ln \frac{\gamma_1}{\gamma_2}$  vs.  $x$  for the system (Methylcyclohexanol + n-Heptane). (Vertical lines indicate error at each exptl. point.)



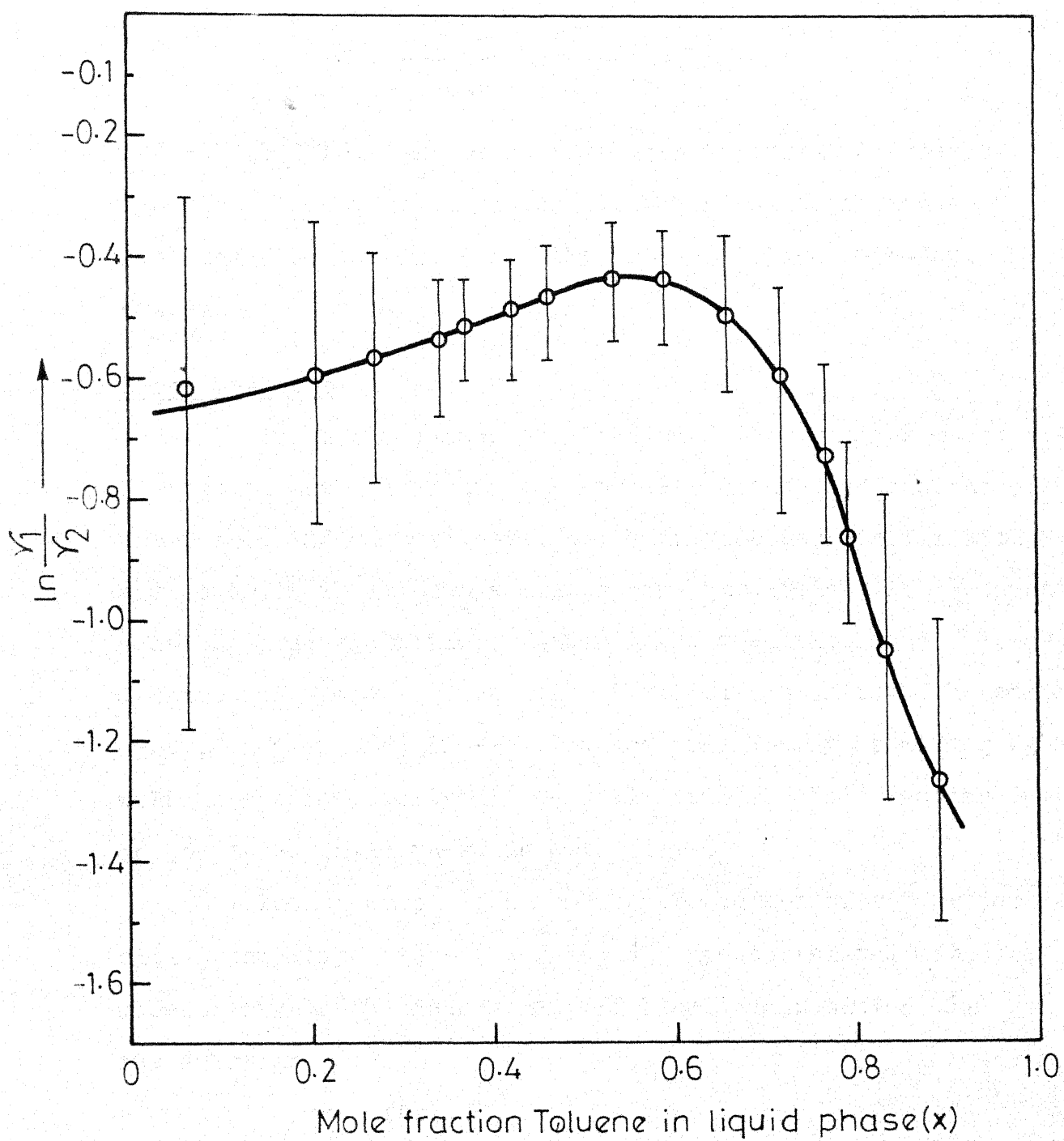


Fig.16 - Plot of  $\ln \frac{p_1}{p_2}$  vs.  $x$  for the system (Toluene + n-Heptanol)  
(Vertical lines indicate error at each exptl. point)

$$J = \frac{150 |P|}{T_{\min}} = \frac{150 \times 63}{383} = 25.4$$

$D-J = 74.5 > 10$ ; Hence Herrington's Criteria for thermodynamic consistency is not satisfied and no significant conclusion can be drawn for the data on toluene + n-Heptanol system.

### Error Analysis

In vapour liquid equilibrium determinations measurable quantities are Temperature, Pressure and the Compositions of the liquid and vapour phases which <sup>are</sup> in true equilibrium with each other. There always exists some uncertainty in the measurement of these quantities. Accordingly the calculated thermodynamic functions e.g. Activity Coefficients of both the components,  $\ln \gamma_1$ ,  $\ln \gamma_2$ ,  $\ln \frac{\gamma_1}{\gamma_2}$ , excess free energy of mixing ( $g^E$ ) will have some uncertainty in their values. This section deals on how to estimate these uncertainties.

The uncertainties in the measurement of vapour composition and temperature ( $\Delta y$  and  $\Delta T$ ) are correlated with the uncertainty in the measurement of liquid composition ( $\Delta x$ ) by the equation

$$y = f(x)$$

$$y = \frac{\delta y}{\delta x} \Delta x \quad \text{where } \frac{\delta y}{\delta x} = \text{slope of } y-x \text{ curve (i)} \\ \text{at the required point}$$

$$T = f(x)$$

$$T = \frac{\delta T}{\delta x} \Delta x \quad \text{where } \frac{\delta T}{\delta x} \text{ is the slope of } x-T \text{ curve at the required point (ii)}$$

The uncertainty in liquid composition  $\Delta x$  is calculated from the difference in Refractive Indices between the two compounds and is given by  $\Delta x = \frac{f}{d_1}$  where  $f$  is the uncertainty in the measurement of Refractive Index (.001) and  $d_1$  is the difference of Refractive Indices of the two compounds at 30°C. The  $\Delta x$  values as calculated from the above equation are 0.0135 (Methylcyclohexanol + n-Heptane) and 0.0129 (Toluene + n-Heptanol).

The uncertainty in the measurement of pressure ( $\Delta P$ ) is taken corresponding to the standard deviation obtained during thermocouple calibration (0.1°C). It has been found from the vapour pressure chart for Analar Benzene that corresponding to the uncertainty of 0.1°C in the temperature measurement, the uncertainty in pressure measurement i.e.  $\Delta P =$  mm.Hg.

It is well known that the activity coefficient of component 1 i.e.  $\gamma_1$  is a function of  $y_1$  (the mole fraction of component 1 in the vapour phase),  $x_1$  (mole fraction of component 1 in the liquid phase) and  $P$  (the experimental pressure); that is

$$\gamma_1 = f(x_1, y_1, P)$$

According to the Taylor's series

$$\Delta \gamma_1 = \left| \frac{\partial \gamma_1}{\partial x_1} \right|_{y_1, P} \Delta x_1 + \left| \frac{\partial \gamma_1}{\partial y_1} \right|_{x_1, P} \Delta y_1 + \left| \frac{\partial \gamma_1}{\partial P} \right|_{x_1, y_1} \Delta P \quad (\text{VI.4})$$

where  $\Delta x_1$ ,  $\Delta y_1$  and  $\Delta P$  denote the uncertainties in the measurement of liquid composition, vapour composition and pressure respectively.

Again  $\gamma_1$  has been defined as  $\gamma_1 = \frac{P_{y_1}}{x_1 P_1^0}$  (VI.5)

where  $P_1^0$  is the vapour pressure of component 1 at the experimental temperature.

Differentiating equation (VI.5)

$$\left| \frac{\delta \gamma_1}{\delta y_1} \right|_{P, x_1} = \frac{P}{x_1 P_1^0} = \frac{\gamma_1}{y_1}$$

$$\left| \frac{\delta \gamma_1}{\delta P} \right|_{x_1, y_1} = \frac{y_1}{x_1 P_1^0} = \frac{\gamma_1}{P} \quad \text{and} \quad \left| \frac{\delta \gamma_1}{\delta x_1} \right|_{y_1, P} = \frac{P_{y_1}}{x_1^2 P_1^0} = \frac{\gamma_1}{x_1}$$

Substituting these values in equation (VI.4)

$$\Delta \gamma_1 = \gamma_1 \left[ \left| \frac{\Delta y_1}{y_1} \right| + \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta x_1}{x_1} \right| \right] \quad (\text{VI.6})$$

Similarly for the component 2,  $\Delta \gamma_2 = \gamma_2 \left[ \left| \frac{\Delta y_2}{y_2} \right| + \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta x_2}{x_2} \right| \right]$  (VI.7)

Uncertainty in  $\ln \gamma_1$  is given by  $\Delta (\ln \gamma_1) = \frac{\Delta \gamma_1}{\gamma_1} = \left| \frac{\Delta y_1}{y_1} \right| + \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta x_1}{x_1} \right|$

Similarly  $\Delta (\ln \gamma_2) = \left| \frac{\Delta y_2}{y_2} \right| + \left| \frac{\Delta P}{P} \right| + \left| \frac{\Delta x_2}{x_2} \right|$

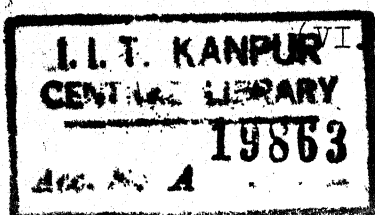
$$\Delta (\ln \frac{\gamma_1}{\gamma_2}) = \left| \Delta (\ln \gamma_1) \right| + \left| \Delta (\ln \gamma_2) \right| = \frac{\Delta \gamma_1}{\gamma_1} + \frac{\Delta \gamma_2}{\gamma_2} \quad (\text{VI.8})$$

The excess free energy of mixing is given by

$$g^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

The uncertainty in  $g^E$  is

$$\Delta g^E = R (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \Delta T + (\ln \gamma_1 \Delta x_1 + \ln \gamma_2 \Delta x_2) T + T (x_1 \frac{\Delta \gamma_1}{\gamma_1} + x_2 \frac{\Delta \gamma_2}{\gamma_2}) \quad (\text{VI.9})$$



In the equations (VI.4) to (VI.9)  $\Delta y$  and  $\Delta T$  are substituted from equations (i) and (ii) respectively. The detailed result of the error analysis for the systems (Methylcyclohexanol (1) + n-Heptane(2)) and (Toluene(1) + n-Heptanol(2)) is given in Tables XI and XII respectively.

These uncertainties are shown in the  $\ln \gamma_i$  vs.  $x_i$  curves in Figures 13 and 14 and  $\ln \frac{\gamma_1}{\gamma_2}$  vs.  $x$  curves in Figures 15 and 16 by vertical lines.

TABLE XI

ERROR ANALYSIS FOR METHYLCYCLOHEXANOL + n-HEPTANE

Mole fraction in liquid phase ( $x_1$ )	$\gamma_1$	$\Delta\gamma_1$	$\gamma_2$	$\Delta\gamma_2$	$\ln \gamma_1$	$\Delta(\ln \gamma_1)$	$\ln \gamma_2$	$\Delta(\ln \gamma_2)$	$\ln \gamma_1 / \gamma_2$	$\Delta(\ln \gamma_1 / \gamma_2)$
0.9847	1.0533	0.1525	1.8439	3.3914	0.0519	0.1448	0.6146	1.8343	-0.5626	1.9791
0.9534	1.0590	0.1511	2.1243	1.1304	0.0573	0.1427	0.7534	0.5321	-0.6961	0.6748
0.9264	1.0468	0.1443	2.2124	0.6924	0.0457	0.1379	0.7941	0.3129	-0.7484	0.4508
0.8801	1.0093	0.1228	2.2667	0.3870	0.0092	0.1217	0.8183	0.1707	-0.8091	0.2924
0.8416	0.9849	0.0999	2.2426	0.2650	0.0152	0.1015	0.8077	0.1181	-0.8229	0.2196
0.7741	0.9045	0.0645	2.0953	0.1536	0.0045	0.0642	0.7397	0.0733	-0.7352	0.1375
0.6859	1.1305	0.0470	1.8125	0.0895	0.1227	0.0416	0.5947	0.0494	-0.4720	0.0910
0.5472	1.2960	0.0648	1.4245	0.0515	0.2593	0.0500	0.3538	0.0362	-0.0946	0.0862
0.4952	1.3322	0.0722	1.3252	0.0440	0.2869	0.0542	0.2816	0.0332	0.0053	0.0874
0.4315	1.4059	0.0812	1.2156	0.0358	0.3407	0.0573	0.1952	0.0295	0.1455	0.0873
0.3403	1.6286	0.1033	1.1176	0.0285	0.4877	0.0635	0.1112	0.0255	0.3765	0.0890
0.2783	1.8960	0.1459	1.0794	0.0259	0.6397	0.0770	0.0764	0.0240	0.5633	0.1019
0.1559	2.4890	0.4305	1.0535	0.0250	0.9119	0.1730	0.0521	0.0238	0.8598	0.1967
0.0688	2.2359	1.0438	1.0371	0.0239	0.8046	0.4668	0.0364	0.0231	0.7682	0.4899

TABLE XII

ERROR ANALYSIS FOR TOLUENE+n-HEPTANOL

Liquid composition ( $x_1$ )	$\gamma_1$	$\Delta\gamma_1$	$\gamma_2$	$\Delta\gamma_2$	$\ln \gamma_1$	$\Delta(\ln \gamma_1)$	$\ln \gamma_2$	$\Delta(\ln \gamma_2)$	$\ln \gamma_1/\gamma_2$	$\Delta(\ln \gamma_1/\gamma_2)$
0.0641	0.5508	0.0232	1.1766	0.0548	-0.5964	0.4052	0.1627	0.0466	-0.7591	0.4518
0.2039	0.6727	0.0882	1.4318	0.0867	-0.3965	0.1312	0.3590	0.0606	-0.7554	0.1918
0.3264	0.8291	0.0646	1.6845	0.1239	-0.1874	0.0779	0.5214	0.0736	-0.7089	0.1514
0.4202	0.9476	0.0535	1.8570	0.1534	-0.0538	0.0565	0.6135	0.0631	-0.6674	0.1396
0.5214	1.0490	0.0435	1.9765	0.1772	0.0478	0.0415	0.6813	0.0897	-0.6335	0.1312
0.5822	1.0887	0.0378	2.0635	0.1856	0.0850	0.0348	0.7244	0.0899	-0.6394	0.1247
0.6516	1.1086	0.0321	2.2385	0.1941	0.1031	0.0289	0.8058	0.0867	-0.7027	0.1156
0.7057	1.1061	0.0283	2.4923	0.2112	0.1009	0.0256	0.9132	0.0847	-0.8123	0.1103
0.7871	1.0791	0.0243	3.1846	0.3085	0.0761	0.0225	1.1583	0.0969	-1.0822	0.1194
0.8321	1.0572	0.0231	3.7803	0.4617	0.0556	0.0219	1.3298	0.1221	-1.2742	0.1440
0.8803	1.033	0.0229	4.5900	0.8375	0.0327	0.0221	1.5239	0.1825	-1.4911	0.2046

## CHAPTER VII

### PREDICTION FROM A SINGLE EXPERIMENTAL DATA

It is often necessary to predict vapour liquid equilibrium properties in the absence of any reliable experimental data. They can be predicted either from the properties of pure components using the molecular theories of solutions, or from limited experimental data on mixtures. Malensinski<sup>32</sup> has suggested a method for prediction of isobaric vapour liquid equilibrium data using a single experimental point. In this method it is assumed that the solution behaves like a regular one and the excess free energy of mixing is related to its composition by

$$g^E = A_{12} x_1 x_2 \quad (\text{VII.1})$$

in which constant  $A_{12}$  is independent of temperature. However, most of the polar-nonpolar mixtures are not regular in nature. Nevertheless if the dependence of temperature on the constant  $A_{12}$  can be assumed to be insignificant over the temperature range in question, then the Malensinski's method would also be applicable for polar-nonpolar mixtures. In this work attempt has been made to test the validity of this assumption for prediction of vapour liquid equilibrium data of hydrocarbon-alcohol systems.

The vapour phase composition as a function of liquid composition for a nonideal liquid solution in equilibrium with nonideal vapour phase is given by

$$Py_1 = P_1^0 x_1 \gamma_1 \exp \frac{(V_1^{\text{OL}} - B_{11})(P - P_1^0) - (2B_{12} - B_{11} - B_{22})y_2^2 P}{RT} \quad (\text{VII.2})$$



and

$$Py_2 = P_2^0 x_2 \gamma_2 \exp \frac{(V_2^{OL} - B_{22})(P - P_2^0) - (2B_{12} - B_{11} - B_{22})y_1^2 P}{RT} \quad (\text{VII.3})$$

where  $B_{11}, B_{22}$  are the second virial coefficients of the components 1 and 2.  $B_{12}$  is the interaction virial coefficient.  $P_1^0$  and  $P_2^0$  are the vapour pressures of pure components at temperature "T";  $\gamma_1$  and  $\gamma_2$  are the activity coefficients of components 1 and 2 respectively in the liquid phase;  $V_1^{OL}$  and  $V_2^{OL}$  are the liquid molar volumes of components 1 and 2 respectively at temperature "T".

The basic equations for isobaric vapour liquid equilibrium is

$$Py_i = P_i' x_i \gamma_i \quad i = 1, 2 \quad (\text{VII.4})$$

where

$$P_i' = p_i^0 \exp \frac{(V_i^{OL} - B_{ii})(P - P_i^0) - \delta_{12} y_j^2 P}{RT} \quad J \neq i \quad (\text{VII.4a})$$

and  $\delta_{12} = (2B_{12} - B_{11} - B_{22})$

The total pressure  $P = \sum Py_i = \sum P_i' x_i \gamma_i$

Dividing both sides by P

$$1 = \sum \frac{P_i'}{P} x_i \gamma_i = \sum \lambda_i x_i \gamma_i \quad \text{where } \lambda_i = \frac{P_i'}{P} \quad (\text{VII.5})$$

$\lambda_i$  is a function of temperature and  $\gamma_i$  is also a function of both temperature and composition. The relation (VII.4) is therefore implicit in T. To obtain vapour composition, the following relation is used,

$$y_r = \frac{\lambda_r x_r \gamma_r}{\sum_{i=1}^2 \lambda_i x_i \gamma_i} \quad (\text{VII.6})$$

Hence to obtain T-x-y relationship from equations (VII.5) and (VII.6) one must know the dependence of activity coefficients on composition and temperature.

The activity coefficients are obtained from the following relation

$$\ln \gamma_i = \frac{1}{RT} \mu_i^E = \frac{1}{RT} \frac{\int (n_T g^E)}{\int n_i}, \quad n_T = \sum n_i \quad (\text{VII.7})$$

Plugging equation (VII.7) in equation (VII.5) one can determine the relationship between T-x and then y-x from equation (VII.6). (T-x) and (y-x) are uniquely determined once the constant  $A_{12}$  in equation (VII.1) is known. Hence the problem of prediction of T-x and y-x relations essentially hinges on the determination of constant  $A_{12}$ .

Equation (VII.5) is implicit in T. This can be overcome by using another form of the equation for the boiling temperature isobar, which can be derived by using the excess free energy of mixing as follows:

$$g^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

Using equation (VII.4)

$$g^E = RT \left( x_1 \ln \frac{P_{y1}}{P_1^* x_1} + x_2 \ln \frac{P_{y2}}{P_2^* x_2} \right)$$

Substituting the values of  $P_1^*$  and  $P_2^*$  from equation (VII.4a)

$$g^E = RT \left( x_1 \ln \frac{P_{y1}}{P_1^0 (\exp u_1) x_1} + x_2 \ln \frac{P_{y2}}{P_2^0 x_2 \exp u_2} \right)$$

where

$$u_i = \frac{(V_i^{OL} - B_{ii})(P - P_i^0) - \delta_{12} y_j^2 P}{RT} \quad (\text{VII.7a})$$

$$\begin{aligned}
 \text{i.e. } g^E &= RT \left[ \left( x_1 \ln \frac{P}{P_1^0} + x_2 \ln \frac{P}{P_2^0} \right) + \left( x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2} \right) \right. \\
 &\quad \left. - (x_1 u_1 + x_2 u_2) \right] \\
 &= RT (V + W - u)
 \end{aligned} \tag{VII.8}$$

$$\text{where } V = x_1 \ln \frac{P}{P_1^0} + x_2 \ln \frac{P}{P_2^0}$$

$$W = x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2} \tag{VII.8a}$$

$$u = x_1 u_1 + x_2 u_2$$

Substituting the value  $g^E$  for  $x_1 = x_2 = 0.5$  in equation (VII.8)

$$A_{12} = 4RT^* (V^* + W^* - u^*) \tag{VII.9}$$

where  $T^*$ ,  $V^*$ ,  $W^*$ ,  $u^*$  denote the respective values at  $x_1 = x_2 = 0.5$ .

In equation (VII.9),  $W^*$  is difficult to calculate since it involves  $y_1$ . For the prediction of actual  $y_1$  at  $x_1 = x_2 = 0.5$  the following method is used.

As a first approximation it is assumed that  $y_1 = y_2 = 0$  at  $x_1 = 0.5$ .  $u_1$  and  $u_2$  are calculated from equation (VII.7a).

$$\text{Now it is known that relative volatility is defined as } \alpha = \frac{P_2^0 \gamma_2 \exp u_2}{P_1^0 \gamma_1 \exp u_1} \tag{VII.10}$$

and the vapour composition of component 1 in equilibrium with the liquid is

$$y_1 = \frac{1}{1 + \alpha}; \quad y_2 = 1 - y_1 \tag{VII.11}$$

This process is iterated until the calculated and experimental value of  $y_1$  at  $x_1 = 0.5$  differ by 2%. This  $y_1$  is taken as the value of  $y_1$  in equilibrium with the liquid of composition  $x_1 = 0.5$ .

$W^*$  is calculated with this value of  $y_1$  and  $y_2$  from equation (VII.8a) and subsequently  $A_{12}$  is calculated from equation (VII.9).

As mentioned earlier, this  $A_{12}$  is assumed to be independent of temperature. With this value of  $A_{12}$  assumed to be constant over the whole composition range, the values of  $y_1$  (mole fraction of component 1 in vapour phase in equilibrium with the liquid) are calculated over the whole composition range of the liquid. The method adopted is as follows:-

$$\text{From Clausius Clapeyron equation } RT \ln \frac{P}{P_i^0} = \Delta S_i (T_i - T) \quad (\text{VII.12})$$

The above relation is true if molar heat of vaporization is assumed to be constant over the temperature interval in question.  $T_i$  denotes the boiling point of pure component  $i$  at pressure  $P$  and  $\Delta S_i$  is the entropy of vaporization.

Now excess free energy of mixing

$$g^E = RT (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) = RT (x_1 \ln \frac{Py_1}{P_1^0 x_1} + x_2 \ln \frac{Py_2}{P_2^0 x_2})$$

Therefore

$$g^E = RT x_1 \ln \frac{P}{P_1^0} + x_2 RT \ln \frac{P}{P_2^0} + RT (x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2}) \quad (\text{VII.13})$$

Plugging equation (VII.12) in equation (VII.13) -

$$g^E = x_1 \Delta S_1^0 (T_1 - T) + x_2 \Delta S_2^0 (T_2 - T) + RT \omega \quad (\text{VII.14})$$

$$\text{where } \omega = (x_1 \ln \frac{y_1}{x_1} + x_2 \ln \frac{y_2}{x_2}) \quad (\text{VII.14a})$$

The equation (VII.14) can now be transformed to the form

$$T = T_1 \frac{x_1 \Delta S_1^0}{\Delta S_0} + T_2 \frac{x_2 \Delta S_2^0}{\Delta S_0} - \frac{g^E}{\Delta S_0} + \frac{RT}{\Delta S_0} \quad (\text{VII.15})$$

$$\Delta S_0 = x_1 \Delta S_1^0 + x_2 \Delta S_2^0$$

is then found by the equation

$$y_2 = \frac{\lambda_2 x_2 \gamma_2}{\lambda_1 x_1 \gamma_1 + \lambda_2 x_2 \gamma_2}$$

where  $\lambda_1, \lambda_2$  have been defined earlier.

This method has been used for our systems i.e. (Methylcyclohexanol(1) + n-Heptane(2)) and (Toluene(1) + n-Heptanol(2)) and the results obtained are tabulated in Tables XIII and XIV respectively.

It is evident from Tables XIII and XIV that for the system (Methylcyclohexanol + n-Heptane) the agreement between experimental and calculated values is satisfactory whereas the same is very poor in (Toluene + n-Heptanol). This may be due to dependence of temperature on the constant which regular solutions ignore. The temperature difference between the two systems are 69 and 63°C respectively. In this wide temperature range it is not wise to assume the constant  $A_{12}$  independent of temperature. Further more Redlich Kister equation involving more than one constant would be better for prediction of vapour liquid equilibrium data of highly nonideal system of hydrocarbon-alcohols. However more experimental data would be necessary for prediction of the constants in the Redlich Kister equation and also their temperature dependence. So conclusion can be drawn that the effect of temperature on the constant  $A_{12}$  has to be taken into account.

TABLE XIII

(METHYLCYCLOHEXANOL(1)+n-HEPTANE(2)).

Liquid Phase composition ( $x_1$ )	Experimental ( $y_1$ )	Calculated ( $y_1$ )	Experimental equilibrium Temperature (°C)	Calculated equilibrium Temperature (°C)
0.9847	0.8810	0.8383	162.29	164.61
0.9534	0.6559	0.6115	152.07	151.68
0.9382	0.5702	0.5373	147.69	147.29
0.9264	0.5126	0.4903	144.54	144.30
0.8801	0.3482	0.3635	134.04	135.28
0.8416	0.2667	0.2996	127.33	130.29
0.7741	0.1951	0.2308	119.08	123.84
0.6849	0.1617	0.1793	113.11	117.51
0.6180	0.1480	0.1546	110.92	113.86
0.5472	0.1330	0.1351	109.65	110.91
0.4992	0.1223	0.1241	109.02	109.36
0.4315	0.1083	0.1103	108.07	107.59
0.3403	0.0934	0.0927	106.23	105.60
0.2139	0.0718	0.0633	102.53	103.01
0.1559	0.0551	0.0530	100.79	102.31
0.1074	0.0367	0.0388	99.63	101.08
0.0688	0.0207	0.0262	99.09	100.12

TABLE XIV

(TOLUENE(1)+n-HEPTANOL(2))

Liquid Phase composition ( $x_1$ )	Experimental ( $y_1$ )	Calculated ( $y_1$ )	Experimental equilibrium temperature (°C)	Calculated equilibrium temperature (°C)
0.0641	0.1323	0.2975	167.94	162.40
0.2039	0.3959	0.6118	155.29	147.27
0.2613	0.4969	0.6869	149.59	142.97
0.3264	0.6011	0.7515	143.20	138.52
0.3552	0.6427	0.7750	140.45	136.72
0.4202	0.7258	0.8197	134.57	132.95
0.4561	0.7647	0.8403	131.55	131.03
0.5204	0.8222	0.8718	126.63	127.87
0.5822	0.8631	0.8970	122.58	125.13
0.6516	0.8943	0.9208	118.85	122.36
0.7057	0.9101	0.9367	116.54	120.39
0.7506	0.9194	0.9434	115.01	119.49
0.7871	0.9258	0.9538	113.99	118.15
0.8321	0.9336	0.9654	112.99	116.54
0.8803	0.9446	0.9767	112.18	114.86

## CHAPTER VIII

### CONCLUSION

Vapour pressure data of Methylcyclohexanol were measured over a pressure range of 200-800 mm.Hg. It is found from Figure 12 that the plot of  $\log P$  vs  $1/t$  is a straight line which means that the data should satisfy Antoine's equation. However, Martin's vapour pressure equation was also found to fit the experimental data and the Martin's constants were found out by regression analysis.

The isobaric vapour liquid equilibrium data for the systems (1) Methylcyclohexanol + n-Heptane and (2) Toluene + n-Heptanol were determined at 760 mm.Hg. It is evident that the T-x-y diagrams (Figures 8 and 10) that both the systems do not form any azeotrope. The activity coefficients of individual components in both the systems were calculated taking vapour phase nonideality into consideration. For the first system the logarithm of activity coefficient of methylcyclohexanol plotted as a function of its liquid phase composition exhibits a maximum at a low composition of methylcyclohexanol whereas logarithm of activity coefficient of n-heptane exhibits a maximum at a high mole fraction of methylcyclohexanol. This kind of behaviour may be due to high degree of nonideality of the system which may be attributed to association of methylcyclohexanol molecules and dipole-induced dipole interaction between methylcyclohexanol and n-Heptane. From the plot of  $\ln \frac{\gamma_1}{\gamma_2}$  vs. x (Figure 15) for this system methylcyclohexanol +



heptane it is found that Herrington's area test for thermodynamic consistency is satisfied. So conclusion can be drawn that isobaric vapour liquid equilibrium data for the system (methylcyclohexanol + n-heptane) are thermodynamically consistent. For the second systems, the logarithm of activity coefficient of toluene plotted as a function of its liquid phase composition (Figure 14) changes its sign from negative to positive whereas the logarithm of activity coefficient of n-heptanol is always positive. As a result  $\ln \frac{\gamma_1}{\gamma_2}$  vs  $x$  for the system toluene + n-heptanol (Figure 16) it is seen that there is no positive area. So it appears that the Herrington's area test for thermodynamic consistency cannot be applied for this system. This may be due to the fact that the heat of mixing for this system is a highly asymmetric function of composition. So it is concluded that unless the heat of mixing data are available as a function of composition the isobaric vapour liquid equilibrium data of this system cannot be tested for thermodynamic consistency.

In the error analysis it has been found that the errors in  $\ln \gamma_1$ ,  $\ln \gamma_2$  and  $\ln \frac{\gamma_1}{\gamma_2}$  for the system methylcyclohexanol + n-heptane are much more than those for the system toluene + n-heptanol, (Figures 13, 14, 15 16). This observation is inspite of the fact that the system methylcyclohexanol + n-heptane followed Herrington's area test whereas the same test failed for toluene + n-heptanol system. This behavior throws a light on the reliability of the vapour liquid equilibrium data published in the literature.

The isobaric vapour liquid equilibrium data are often predicted over the whole composition range from a single experimental data by using Malessinski's method. In this method it is assumed that the solution behaves like a regular one and hence the constant  $A_{12}$  (Chapter VII) is independent of temperature. However, most of the polar nonpolar systems are not regular solutions. To test whether the constant  $A_{12}$  can be assumed to be independent of temperature over the temperature range in question Malessinski's method has been applied for the systems.

It is evident from Tables XIII and XIV that for the system methylcyclohexanol + n-heptane the agreement is somewhat satisfactory whereas for the system (toluene +n-heptanol}the agreement is very poor. So it can be concluded that the effect of temperature on the constant  $A_{12}$  has to be taken into account. However, Redlich Kister equation for the excess free energy of mixing involving more than one constant would probably be better for prediction of vapour liquid equilibrium data of systems of hydrocarbon-alcohol. In that case more than one experimental data would be needed for determining the constants of the equation and also their temperature dependence.

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## CHAPTER IX

### RECOMMENDATION

From the present experimental analysis it is evident that the hydrocarbon + alcohol mixtures are highly nonideal in nature and they do not form regular solutions. So excess properties such as excess heat of mixing, excess volume of mixing, excess entropy of mixing, excess free energy of mixing as a function of composition are necessary for complete understanding of the mixtures. Excess free energy of mixing could be calculated from the isothermal vapour liquid equilibrium data over a temperature range using the same experimental set-up. Isothermal vapour liquid equilibrium data could also be estimated from isobaric data incorporating some temperature dependence of the constants in the Redlich Kister equation.

The present experimental set-up could be used to determine isobaric as well as isothermal multicomponent vapour liquid equilibrium data of polar nonpolar systems. The multicomponent vapour liquid equilibrium data can also be predicted from the binary experimental data using Prausnitz's method. These predicted values can be compared with the experimental data for testing the validity of the method. Since multicomponent vapour liquid equilibrium data are quite useful in industry, this work is of significant importance.

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APPENDIX 1CALIBRATION OF THERMOCOUPLES

Accurate measurement of temperature (both equilibrium temperature and the boiling point of the ebulliometric liquid), was carried out by copper constantan (cu = 60%, Ni = 40%) thermocouples calibrated against a standard platinum resistance thermometer having a precision of           The emf reading was taken by means of a Honeywell Potentiometer having a precision of           The copper constantan thermocouples were chosen because of the high thermal conductivity and low oxygen content of copper and the high operating range of 0° to 350°C. A copper constantan thermocouple wire of length           is taken. One end of the copper and constantan wires is fused with each other which forms the hot junction of the thermocouple. The other ends of the copper and constantan wire were fused to two thick copper wires. The other ends of the copper extension leads were connected to the potentiometer for emf measurement. Thick copper wires were used so that the resistance in the line is minimum. The junctions of copper and constantan wires with the two thick copper wires form the cold junctions of the thermocouple. These cold junctions were maintained at 0°C by placing them in a mixture of crushed ice and water in a Dewar flask. Care was taken to avoid air pockets in the ice-water mixture and from time to time water was replaced by new water. The hot junction of the thermocouple is placed inside a shield. The shield is a glass tube closed at one end. Mercury is

kept inside the shield to improve heat transfer from the thermowell to the hot junction of the thermocouple.

It is well known that emf developed between hot and cold junctions of a thermocouple ( $E$ ) is a function of temperature that is to be measured. The relationship between emf and temperature is given by a polynomial in the form:  $E = a + bt + ct^2 + \dots$ . This emf is measured by the potentiometer. It is necessary to have a chart of emf vs. temperature for thermocouple which will give directly the temperature to be measured from a knowledge of the emf across the hot and cold junctions of the thermocouple. The calibration of thermocouple involves preparation of this chart.

The schematic diagram of the set-up used for this purpose is shown in Figure 17.

A pure liquid (whose vapour pressure data are known) is boiled in the bulb ( $B$ ) of the vapor jacket ( $V$ ). The bulb is heated by a heating mantle ( $M$ ) which is controlled by means of variac. The vapour evolving from the boiling liquid condenses along the wall of the jacket ( $V$ ) and thus maintaining the jacket at the boiling temperature of the pure liquid. To ensure constant temperature in the jacket pressure is maintained constant in the vapour jacket. To prevent the heat loss to the surroundings the jacket is provided with a silvered double walled evacuated chamber with two diametrically opposite viewing slits. In addition, the connecting tubes ( $L_1, L$  etc) are properly insulated by glass wool. The corks ( $C_1$ ) and ( $C_2$ ) are used to close the jacket at both ends. A  $\frac{1}{2}$  inch layer of mercury

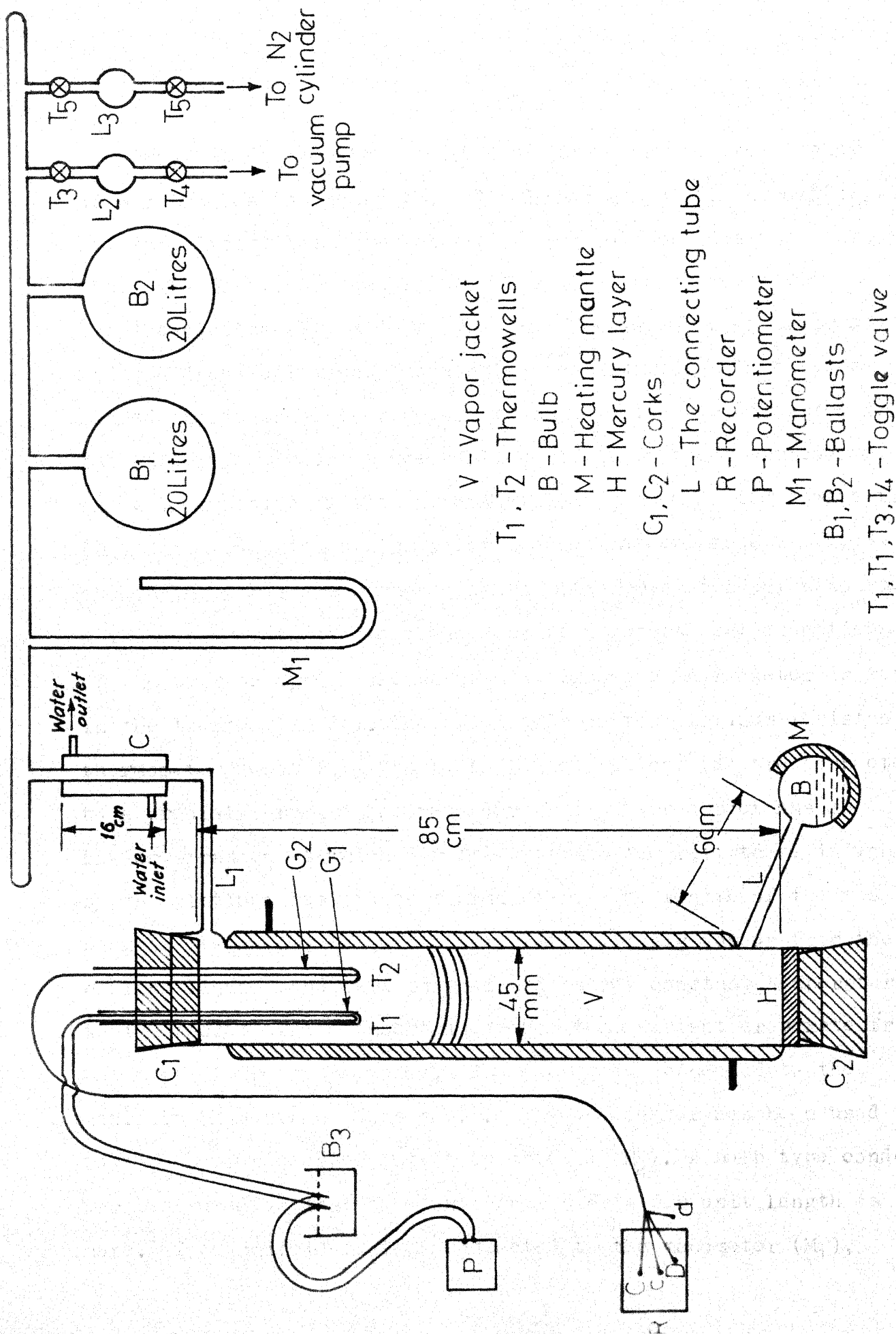


Fig.17 - Calibration of Thermocouples



provides a seal over the cork( $C_2$ ) so as to prevent the leakage of air bubbles to the system. Two holes are bored in cork( $C_1$ ) and two glass tubes (both closed at one end) are inserted through the holes inside the jacket(V). These two glass tubes act as the thermowells ( $T_1$ ) and ( $T_2$ ) for the hot junction of thermocouple and platinum resistance thermometer respectively. Mercury is placed inside these thermowells to improve the heat transfer from the condensed vapour of the boiling liquid to the thermocouple. The cold junction of the thermocouple is placed in the deware flask ( $B_3$ ) which contains a mixture of crushed ice and water. The connecting wires are attached to the high precision potentiometer(P) which measures the emf developed between hot and cold junctions of the thermocouple. The platinum resistance thermometer is kept in the thermowell ( $T_1$ ). The other ends of the platinum resistance thermometer denoted by the leads (C)(c), (D) and (d) are connected to a precision resistance recorder (R). The recorder has an inking arrangement which directly records the resistance indicated by the platinum resistance thermometer. The length of the two thermowells should be sufficient so that rising vapour from the boiling liquid condenses on them and steady constant temperature in the jacket can be ascertained from the constant drop rate from the tips of the thermowells. The jacket is connected to the manifold ( $M_2$ ) via condenser (C). This condenser has been used so that no vapour escapes into the manifold ( $M_2$ ). A bulb type condenser has been used so that the condensation area per unit length is more. The manifold ( $M_2$ ) is connected to the manometer ( $M_1$ ),

ballasts ( $B_1$ ) and ( $B_2$ ) and the lines ( $L_2$ ) and ( $L_3$ ). The manometer ( $M_1$ ) reads the system pressure. The ballast consists of two 20 litres flasks which dampen the pressure fluctuation in the system. Lines ( $L_2$ ) and ( $L_3$ ) are used to change the vacuum in the system. ( $L_2$ ) being connected to the vacuum pump and ( $L_3$ ) to the  $N_2$  cylinder. Toggle valves ( $T_3$ )( $T_4$ )( $T_5$ ) and ( $T_6$ ) are used to effect slight fluctuation of pressure in the system, their opening and closing times being very small.

In the calibration of thermocouples the main aim is to maintain different constant temperatures in the jacket and to read the emf of the thermocouple by the potentiometer and the resistance of the platinum resistance thermometer by the recorder (R) at these temperatures. This is done by maintaining different pressures in the system via the lines ( $L_2$ ) and ( $L_3$ ). When the temperature becomes steady, the resistance of the platinum wire in the platinum resistance thermometer (as indicated by the recorder) and the emf between the hot and cold junctions of the thermocouple (as indicated by the potentiometer P) are noted. It is well known that resistance at any temperature (T) is given by

$$R_t = R_0 (1 + At + Bt^2)$$

where  $R_0$  = Resistance at  $0^\circ\text{C}$  :

A = Constant =

B = Constant =

With the knowledge of  $R_0$ , A and B it is possible to prepare a chart of Resistance vs. Temperature for the platinum resistance

thermometer. Since a chart of resistance vs. temperature is available, emf vs. temperature for the thermocouple can be known since both resistance and emf have been taken at the same temperature.

These emf. temperature data are subjected to regression analysis to find out the standard deviation and optimum number of constants of the polynomial relating emf and temperature (i.e. in  $t = a + bE + cE^2 + \dots$ , a, b, c etc.). The optimum number of constants are found in succession until the experimental data fall within 95% confidence limit of the polynomial.

The pure liquids used for calibration are (i) Analar Toluene for the temperature range 50°-110°C, (ii) Analar bromobenzene for the temperature range 110°-157°C, and (iii) pure naphthalene for the temperature range 157°-180°C.

The resistance emf. temperature data for the thermocouples (TC<sub>1</sub>) and (TC<sub>2</sub>) have been shown in Tables XV(a) and XV(b) respectively.

TABLE XV(a)

Liquid used in vapour jacket	Thermo-couple emf(milli-volts)	Resistance recorded by platinum resistance thermometer	Temperature from resistance-Temp. chart (°C)	Temperature calculated from polynomial (°C)
Analar Toluene	1.959	30.506	48.65	48.609
	3.031	32.974	73.26	73.280
	3.990	35.105	94.730	94.679
Bromo-benzene	4.962	37.129	115.22	115.204
	5.710	38.642	130.61	130.512
	6.358	39.249	143.70	143.76
	6.507	40.229	146.84	146.793
	6.660	40.520	149.83	149.880
	6.968	41.111	155.90	155.930

The standard deviation is  $0.08432^{\circ}\text{C}$

The constants of the polynomial are  $A = -9.777$

$B = 46.750$

$C = -17.297$

$D = 6.5473$

$E = -1.335$

$F = 1.364$

$G = -0.00549$

TABLE XV(b)

Liquid used in vapour jacket	Thermo-couple emf(milli-volts)	Resistance recorded by platinum resistance thermometer	Temperature from resistance -Temp. chart (°C)	Temperature calculated from polynomial(°C)
Analar Toluene	2.048	30.715	50.740	50.665
	3.241	33.450	78.070	77.978
	4.215	35.538	99.100	99.283
Analar bromo-benzene	5.164	37.522	119.22	119.321
	5.710	38.642	130.61	130.570
	6.357	39.925	143.73	143.690
	6.963	41.111	155.90	155.870
Naphthalene	7.380	41.891	163.89	164.050
	7.821	42.743	172.690	172.690
	8.323	43.698	182.590	182.519

The standard deviation is 0.08602°C

The constants of the polynomial are A = -0.03316

B = 26.0937

C = -0.7037

D = 0.02450

## APPENDIX 2

### CALIBRATION OF REFRACTOMETER

After the attainment of equilibrium in the experimental set-up the vapour and liquid samples are withdrawn and analyzed for composition by a "Bausch and Lomb" refractometer. Hence the refractometer has to be calibrated against the composition of the mixture to be studied. In the present work the mixtures of Methylcyclohexanol + n-Heptane and Toluene + n-Heptanol have been studied and separate calibration charts have been made for them.

During calibration the refractive indices of the mixtures are measured for several known compositions at a constant temperature. A clean corked sampling tube is taken and weighed in a Mettler's balance. 0.1 cc of one of the components is taken in the sampling tube and the latter is weighed again. Now 1.4 cc of the 2nd component is added to the sampling tube and the latter along with the mixture is weighed. The mole fraction of component 1 in the mixture is calculated as

$$m = \frac{(W_2 - W_1)/M_1}{(W_2 - W_1)/M_1 + (W_3 - W_2)/M_2}$$

where  $W_1$  = weight of empty sampling tube

$W_2$  = weight of empty sampling tube + component 1

$W_3$  = weight of empty sampling tube + mixture

$M_1, M_2$  = are the molecular weights of components 1 and 2 respectively.

The total volume of the mixture (1.5 cc) is kept constant and the proportion of the components 1 and 2 is varied (.2 cc of 1 + 1.3 cc

of 2 and so on). The same procedure is repeated. Thus a large number of mixtures with different mole fractions of component 1 is prepared. The refractive indices of these mixtures are measured in a "Bausch and Lomb" refractometer. Although the refractometer could read upto 4 significant decimal places the refractive index was reproducible only upto 0.001. With this accuracy the mole fraction was reproducible upto 0.0135 (methylcyclohexanol + n-Heptane) and 0.0129 (Toluene + n-Heptanol). Precaution has to be taken so that the temperature in the prism remains constant since the fluctuation of temperature will cause a large error in refractive index. The constant temperature was maintain in the prism by circulating water from a thermostat control water bath. The refractive index composition data for (methylcyclohexanol + n-heptane) and (Toluene + n-heptanol) systems are reported at  $(30 \pm 0.1^{\circ}\text{C})$  in Table XVI. It was not difficult to maintain  $30^{\circ}\text{C}$  in the water bath for the system (Toluene +n-heptanol since the then room temperature was about  $20\text{--}25^{\circ}\text{C}$  while it posed some problem for the other system as the then room temperature was about  $32\text{--}35^{\circ}\text{C}$ . This problem was eliminated by adding ice to the bath once in a while as this helped in bringing down the temperature to  $30^{\circ}\text{C}$ . The refractive index composition data for the systems (Methylcyclohexanol + n-heptane) and (Toluene + n-heptanol) are given in Tables XVI(a) and XVI(b) respectively.

TABLE XVI(a)SYSTEM: METHYLCYCLOHEXANOL(1)+n-HEPTANE(2)

Liquid composition ( $x_1$ )	Refractive index at $30 \pm 0.1^\circ\text{C}$
0.00	1.3821
0.1790	1.3938
0.5390	1.4197
0.7050	1.4331
0.7560	1.4371
0.8480	1.4446
0.9434	1.4526
1.0000	1.4564

TABLE XVI(b)SYSTEM: TOLUENE + N-HEPTANOL

Liquid composition ( $x_1$ )	Refractive Index at $30 \pm 0.1^\circ\text{C}$
0.00	1.4160
0.1971	1.4276
0.3101	1.4361
0.5600	1.4530
0.7100	1.4630
0.8590	1.4760
0.9460	1.4880
1.00	1.4930



These refractive index mole fraction data are subjected to regression analysis to find out the standard deviation in composition and the constants of the polynomial relating mole-fraction to refractive index (i.e  $x = a + bR + cR^2 + \dots$ , a,b,c etc). The optimum number of constants are found in succession until the experimental data fall within 95% confidence limit of the polynomial.

These constants are:

Methylcyclohexanol+n-Heptane

$$A = -66.424$$

$$B = 81.114$$

$$C = -23.884$$

Toluene + n-Heptanol

$$A = -141.094$$

$$B = 181.683$$

$$C = -57.941$$

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APPENDIX 3THERMODYNAMIC RELATIONS AND SOME BASIC EQUATIONS  
FOR THE DETERMINATION OF SOME THERMODYNAMIC PRO-  
PERTIES(i) Gibbs Duhem Equation

It is well known that if  $M$  is an extensive property of a mixture, then  $M$  is a function of temperature, pressure and the number of moles of different ingredients in the mixture.

$$\text{i.e. } M = f(T, P, n_1, n_2, \dots)$$

$$dM = \left(\frac{\partial M}{\partial T}\right)_{P, \text{all } n} dT + \left(\frac{\partial M}{\partial P}\right)_{T, \text{all } n} dP + \sum_i \left(\frac{\partial M}{\partial n_i}\right)_{T, P, n_j} dn_i \quad (1)$$

If it is assumed that  $M$  is the Gibbs free energy  $G$ .

then  $\left(\frac{\partial G}{\partial T}\right)_{P, \text{all } n} = -S$ ,  $\left(\frac{\partial G}{\partial P}\right)_{T, \text{all } n} = V$ ,  $\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} = \mu_i$

Substituting these relations in equation (1)

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (2)$$

Again the extensive property " $G$ " is related to the partial molar properties by Euler's theorem, i.e.

$$G = \sum_i \mu_i n_i$$

or  $dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i \quad (3)$

Comparing equations (2) and (3)  $-SdT + VdP - \sum_i n_i d\mu_i = 0$

or  $SdT - VdP + \sum_i n_i d\mu_i = 0$

This equation is known as Gibbs's Duhem equation and this is the fundamental equation in the thermodynamics of solutions.

(ii) The equilibrium between vapour and liquid:

According to the equilibrium condition, the chemical potentials of the  $i$ th component in the liquid and vapour phase must be equal.

$$\text{i.e. } \mu_i^L(T, P, x) = \mu_i^V(T, P, y)$$

The chemical potential of the  $i$ th component in the vapour phase

$$\text{can be written as } \mu_i^V = \mu_i^V(T) + RT \ln f_i \quad (3a)$$

where  $f_i$  = the fugacity of the  $i$ th component given by

$$RT \ln \frac{f_i}{y_i P} = \int_0^P (v_i^V - \frac{RT}{P}) dP \quad (4)$$

$$\text{Substituting (4) in (3a) } = \mu_i^V(T) + RT \ln y_i P + \int_0^P (v_i^V - \frac{RT}{P}) dP \quad (5)$$

Similarly for the pure vapour of  $i$ th component

$$\mu_i^{\text{ov}}(T, p_i^0) = \mu_i^V(T) + RT \ln P_i^0 + \int_0^{P_i^0} (v_i^{\text{ov}} - \frac{RT}{P}) dP \quad (6)$$

Subtracting equation (5) and (6)

$$\mu_i^V - \mu_i^{\text{ov}} = RT \ln \frac{Py_i}{P_i^0} + \int_0^P (v_i^V - \frac{RT}{P}) dP - \int_0^{P_i^0} (v_i^{\text{ov}} - \frac{RT}{P}) dP \quad (7)$$

Similarly it can be shown that the difference between the chemical potentials of component  $i$  in the solution and in the pure liquid is

$$\mu_i^L(T, P, x) - \mu_i^{\text{ol}}(T, p_i^0) = RT \ln x_i \gamma_i + \int_{P_i^0}^P v_i^L dP \quad (8)$$

where  $v_i^{\text{ol}}$  is the special volume of pure liquid  $i$  at the temperature  $T$ .

For the equilibrium condition equations (7) and (8) are to be identical. Applying virial equation of state in this master

equation, it can be shown

$$\gamma_1 = \frac{Py_1}{P_1^0 x_1} \exp \frac{(B_{11} - v_1^{OL})(P - P_1^0) + (2B_{12} - B_{11} - B_{22})y_2^2 P}{RT} \quad (10)$$

$$\gamma_2 = \frac{Py_2}{P_2^0 x_2} \exp \frac{(B_{22} - v_2^{OL})(P - P_2^0) + (2B_{12} - B_{11} - B_{22})y_1^2 P}{RT} \quad (11)$$

Equations (10) and (11) are used to calculate the activity coefficients of components 1 and 2 i.e.  $\gamma_1$  and  $\gamma_2$  from a knowledge of vapour liquid equilibrium data.

### (iii) Virial Coefficients;

Most of the real gases are nonideal in nature. The non-ideality in gases is studied in the form of virial equation of state which reads as

$$\frac{PV}{RT} = Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$

The coefficients B, C...are called virial coefficients where B denotes the second virial coefficient, C the third virial coefficient and so on. The virial coefficients depict the molecular interaction and as a result can be predicted from a knowledge of intermolecular force. Kreglawski<sup>28</sup> has used two-step square well potential energy function to find out the second virial coefficient.

From this concept it can be shown that

$$\frac{\beta}{bV^*} = 1(R_1 - 1)(e^{-\frac{u}{kT}} - 1) - (R_2 - R_1)(e^{-su/kT} - 1)$$

where  $R_1 = \left[1 + \frac{S}{(V^*)^{1/3}}\right]^3$ ;  $R_2 = \left[1 + \left(\frac{V_o^*}{V^*}\right)^{1/3}\right]^3$

where  $E^*$  is the activation energy at  $T_r = 0.6$

$V^*$  is the molar volume at  $T_r = 0.6$

The packing parameter B and parameter S can be related to  $E^*$  and  $v^*$ .

(iv) Calculation of Specific Volume and Molar Volume:

The densities of the liquids under investigation have been calculated by Yen and Wood's<sup>25</sup> equation. The equation is as follows:

$$\rho_r = \frac{\rho_s}{\rho_c} = 1 + A(1-Tr)^{1/3} + B(1-Tr)^{2/3} + D(1-Tr)^{4/3}$$

where constants A, B and D can be calculated from a knowledge of critical compressibility factor using some empirical relations. The molar volume =  $\frac{M}{\rho_s}$  where M is the molecular weight.

(v) Calculation of Critical Properties:

Critical temperature is calculated from Guldberg rule<sup>20</sup> which states  $T_c = \frac{T_b}{\theta}$ , where  $T_b$  is the boiling point.

$$\theta = .574 + \sum \Delta T \text{ (Riedel)}$$

$\sum \Delta T$  is calculated by summing atomic and structural constants which represent the component parts of the molecule.

Critical pressure is calculated from the model proposed by Riedel<sup>20</sup> which states

$$P_c = \frac{M}{(\phi + 0.33)^2} \quad \text{where } M \text{ is the molecular weight}$$

$\phi$  is the additive constant  
determined from molecular  
structure.

Critical compressibility factor  $Z_c = \frac{P_c V_c}{RT_c}$

(vi) Calculation of  $E^*$ 

The activation energy at  $Tr = 0.6$  ( $E^*$ ) is calculated from the heat of vaporization at  $Tr=0.6$ .

According to Riedel<sup>20</sup>, the latent heat of vaporization at normal boiling point is given by

$$\Delta H_{vb} = \frac{RT_c T_b \ln P_c}{T_c - T_b} \quad \text{where } P_c, T_c \text{ denote critical properties and } T_b \text{ is the normal boiling point.}$$

The latent heat of vaporization at  $Tr = 0.6$  is given by<sup>20</sup>

$$\Delta H_v = \Delta H_{vb} \left( \frac{1-Tr}{1-T_{br}} \right)^{0.38} \quad \text{where } T_{br} \text{ denotes the reduced temperature corresponding to NBP.}$$

Activation energy at  $Tr = 0.6$  is given by<sup>20</sup>  $E^* = (\Delta H_v - RT)$

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APPENDIX 4PHYSICAL PROPERTIES OF PURE SUBSTANCES(I) n-Heptane

The vapour pressure at different temperatures was calculated from Antoine's equation. The virial coefficient data as a function of temperature were available from literature. These data were subjected to regression Analysis to fit a model between  $B_v$  and  $T$ . The critical properties<sup>33</sup> were available in the literature.<sup>33</sup>

(II) Methylcyclohexanol

The experimentally determines vapour pressure data were found to fit Martin's equation which states

$$\log P = A + B/T + CT + DT^2 + ET^3 + F \log(G-T)$$

The constants A,B,C,D,E,F and G were determined.

The critical properties were predicted from the relations given in part(V) of Appendix 3. These critical properties were used to find out  $v^*$  from Yen & Wood's Equation<sup>25</sup> and  $E^*$  from the relation given in part (VI) of Appendix 3. With the knowledge of  $E^*$  and  $v^*$ , virial coefficient as a function of temperature was determined by Kreglowski's model.<sup>28</sup>

(III) Toluene

The vapour pressure at different temperatures was calculated by Antoine's equation. The critical properties<sup>33</sup> and virial coefficient as a function of temperature was obtained from literature.

(IV) N-Heptanol

The vapour pressure at different temperatures were calculated by Antoine's equation. The critical properties were predicted from the relations given in part (V) of Appendix 3. The critical properties were used to find out  $v^*$  from Yen and Wood's equation<sup>25</sup> and  $E^*$  from the relation given in part (VI) of Appendix 3. With the knowledge of  $E^*$  and  $v^*$ , virial coefficient as a function of temperature was determined by Kreglowski's model.<sup>28</sup>

The physical properties of all these compounds are tabulated in Table XVII.



TABLE XVII

Name of the Compound	Va pour Pressure (mm)	Critical Properties			Second virial coefficient ( $B_v$ ): $B_v$ at MBP and constants A, B, C, etc. in the equation $B_v = A + BT + CT^2 + \dots$	Refractive Index at $30 \pm 0.1^\circ\text{C}$	Boiling Point at 760 mm. Hg. ( $^\circ\text{C}$ )
		$V_c$ (cc/g.mole)	$T_c$ ( $^\circ\text{K}$ )	$Z_c$			
n-Heptane	Antoine's Cons.						
	A = 6.91528	426.0	540.3	0.259	$B_v = -13679.274$	1.3821	98.428
	B = 1275.626				B = 53.27721		
	C = 217.755				C = -0.05532		
Methylcyclohexanol	Martin's Const.						
	A = .77898216	383.0	620.0	0.281	$B_v = 98109.325$	1.4564	167.835
	B = 2368.51				B = 550.255		
	C = .022726				C = -1.0869		
	D = .729E-04				D = 0.73802E-03		
	E = -.145E-06						
	F = -8.11365						
	G = 602.15						
Analar Toluene	Antoine's const.						
	A = 6.95334	316.0	592.0	0.271	$B_v = -5234.404$	1.4160	110.82
	B = 1343.943				A = -5234.404		
	C = 219.377				B = 10.4575		
n-Heptanol	Antoine's Consts						
	A = 6.6476	430.0	633.1	0.243	$B_v = -4532.2404$	1.4932	173.42
	B = 1140.64				A = -4532.2404		
	C = 126.56				B = -2.3157		
					C = .05583		
					D = -.7235E-04		